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(54) ELASTIC SUBSTANTIALLY LINEAR OLEFIN POLYMERS

ELASTISCHE, IM WESENTLICHEN LINEARE OLEFINPOLYMERE

POLYMERES OLEFINIQUES ELASTIQUES SENSIBLEMENT LINEAIRES

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Description

Field of the Invention

This invention relates to elastic substantially linear olefin polymers having improved processability, e.g., low susceptibility to melt fracture, even under high shear stress conditions. Such substantially linear olefin polymers have a critical shear rate at the onset of surface melt fracture substantially higher than, and a processing index substantially less than, that of a linear polyolefin at the same molecular weight distribution and melt index.

Background of the Invention

Molecular weight distribution (MWD), or polydispersity, is a well known variable in polymers. The molecular weight distribution, sometimes described as the ratio of weight average molecular weight (M_w) to number average molecular weight (M_n) (i.e., M_w/M_n) can be measured directly, e.g., by gel permeation chromatography techniques, or more routinely, by measuring I_{10}/I_2 ratio, as described in ASTM D-1238. For linear polyolefins, especially linear polyethylene, it is well known that as M_w/M_n increases, I_{10}/I_2 also increases.

John Dealy in "Melt Rheology and Its Role in Plastics Processing" (Van Nostrand Reinhold, 1990) page 597 discloses that ASTM D-1238 is employed with different loads in order to obtain an estimate of the shear rate dependence of melt viscosity, which is sensitive to weight average molecular weight (M_w) and number average molecular weight (M_n).

Bersted in Journal of Applied Polymer Science Vol. 19, page 2167-2177 (1975) theorized the relationship between molecular weight distribution and steady shear melt viscosity for linear polymer systems. He also showed that the broader MWD material exhibits a higher shear rate or shear stress dependency.

Ramamurthy in Journal of Rheology, 30(2), 337-357 (1986), and Moynihan, Baird and Ramanathan in Journal of Non-Newtonian Fluid Mechanics, 36, 255-263 (1990), both disclose that the onset of sharkskin (i.e., melt fracture) for linear low density polyethylene (LLDPE) occurs at an apparent shear stress of 10-14 N/cm² ($1-1.4 \times 10^6$ dyne/cm²), which was observed to be coincident with the change in slope of the flow curve. Ramamurthy also discloses that the onset of surface melt fracture or of gross melt fracture for high pressure low density polyethylene (HP-LDPE) occurs at an apparent shear stress of about 0.13 MPa (1.3×10^6 dynes/cm²).

Kalika and Denn in Journal of Rheology, 31, 815-834 (1987) confirmed the surface defects or sharkskin phenomena for LLDPE, but the results of their work determined a critical shear stress of 23 N/cm² (2.3×10^6 dyne/cm²), significantly higher than that found by Ramamurthy and Moynihan et al. International Patent Application WO 90/03414, published April 5, 1990, discloses linear ethylene interpolymers with narrow molecular weight distribution and narrow short chain branching distributions (SCBDs). The melt processability of the interpolymers blends is controlled by blending different molecular weight interpolymers having different narrow molecular weight distributions and different SCBDs.

Exxon Chemical Company, in the Preprints of Polyolefins VII International Conference, page 45-66, February 24-27 1991, disclose that the narrow molecular weight distribution (NMWD) resins produced by their EXXPOL™ technology have higher melt viscosity and lower melt strength than conventional Ziegler resins at the same melt index. In a recent publication, Exxon Chemical Company has also taught that NMWD polymers made using a single site catalyst create the potential for melt fracture ("New Specialty Linear Polymers (SLP) For Power Cables," by Monica Hendewerk and Lawrence Spenadel, presented at IEEE meeting in Dallas, Texas, September, 1991). In a similar vein, in "A New Family of Linear Ethylene Polymers Provides Enhanced Sealing Performance" by Dirk G. F. Van der Sanden and Richard W. Halle, (February 1992 Tappi Journal), Exxon Chemical Company has also taught that the molecular weight distribution of a polymer is described by the polymers melt index ratio (i.e., I_{10}/I_2) and that their new narrow molecular weight distribution polymers made using a single site catalyst are "linear backbone resins containing no functional or long chain branches."

WO-A-90/07526, corresponding to EP-A-0 495 099, discloses ethylene copolymers obtained from a process wherein ethylene and optionally other monomers are contacted with a catalyst system based on hafnocene and zirconocene catalysts. The product polymer is in fact a blend of polymers having a narrow molecular weight distribution with values of from 1.2 to 4 and a melt flow ratio MFR_{10}/MFR_2 of 8 to 50.

Previously known narrow molecular weight distribution linear polymers disadvantageously possessed low shear sensitivity or low I_{10}/I_2 value, which limits the extrudability of such polymers. Additionally, such polymers possessed low melt elasticity, causing problems in melt fabrication such as film forming processes or blow molding processes (e.g., sustaining a bubble in the blown film process, or sag in the blow molding process etc.). Finally, such resins also experienced melt fracture surface properties at relatively low extrusion rates thereby processing unacceptably.

Summary of the Invention

Olefin polymers characterized as substantially linear olefin polymers have now been discovered which have unusual properties, including an unusual combination of properties, which leads to enhanced processability of the novel polymers. The substantially linear olefin polymers have the processability similar to highly branched low density polyethylene (LDPE), but the strength and toughness of linear low density polyethylene (LLDPE). However, the novel substantially linear olefin polymers are distinctly different from traditional Ziegler polymerized heterogeneous polymers (e.g., LLDPE) and are also different from traditional free radical/high pressure polymerized LDPE. Surprisingly, the novel substantially linear olefin polymers are also different from homogeneous olefin polymers having a uniform branching distribution.

More particular, the present invention relates to an olefin polymer characterized in that the olefin polymer is an olefin polymer, substituted with 0.01 to 3 long chain branches per 1000 carbons of the backbone, having a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer that does not have long chain branches at about the same I_2 and M_w/M_n , and has a single melting point as determined by differential scanning calorimetry.

Further, the invention relates to a process for the preparation of an olefin polymer substituted with 0.01 to 3 long chain branches per 1000 carbons of the backbone, having a melt flow ratio $I_{10}/I_2 \geq 5.63$, a molecular weight distribution M_w/M_n defined by the equation $M_w/M_n \leq I_{10}/I_2 - 4.63$, and a single melting point as determined by differential scanning calorimetry, said process being characterized as a continuous process comprising continuously contacting one or more C_2-C_{20} olefins with a catalyst composition under polymerization conditions, wherein said catalyst composition is characterized as:

- a) one metal coordination complex comprising a metal atom of groups 3-10 or the Lanthanide series of the Periodic Table of the Elements and a delocalized π -bonded moiety substituted with a constrain inducing moiety, said complex having a constrained geometry about the metal atom such that the angle at the metal atom between the centroid of the delocalized, substituted π -bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar π -bonded moiety lacking in such constrain-inducing substituent, and provided further that for such complexes comprising more than one delocalized, substituted π -bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted π -bonded moiety, and
- b) an activating cocatalyst.

In addition, the invention relates to a composition comprising the substantially linear olefin polymer of the invention and at least one other natural or synthetic polymer, as well as fabricated articles comprising the substantially linear olefin polymer of the invention.

The substantially linear olefin polymers of the invention preferably have:

- a) a melt flow ratio, $I_{10}/I_2 \geq 5.63$, and
- b) a molecular weight distribution, M_w/M_n , defined by the equation:

$$M_w/M_n \leq (I_{10}/I_2) - 4.63.$$

Further, the critical shear stress at onset of gross melt fracture is preferably greater than 40 N/cm² (4×10^6 dyne/cm²).

In another embodiment, the substantially linear olefin polymers have:

- a) a melt flow ratio, $I_{10}/I_2 \geq 5.63$, and
- b) a molecular weight distribution, M_w/M_n of from 1.5 to 2.5.

In still another embodiment, the substantially linear olefin polymers have:

- a) a melt flow ratio, $I_{10}/I_2 \geq 5.63$,
- b) a molecular weight distribution, M_w/M_n of from 1.5 to 2.5, and
- c) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer at about the same I_2 and M_w/M_n .

The substantially linear olefin polymer preferably has:

- (a) from 0.01 to 3 long chain branches/1000 carbons along the polymer backbone and
- (b) a critical shear stress at onset of gross melt fracture of greater than 40 N/cm² (4×10^6 dynes/cm²).

The substantially linear olefin polymer can also have:

- (a) from about 0.01 to about 3 long chain branches/1000 carbons along the polymer backbone and
- (b) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer at about the same I_2 and M_w/M_n .

And in still another embodiment, the olefin polymer can be characterized as a substantially linear olefin polymer having:

- (a) from 0.01 to 3 long chain branches/1000 carbons along the polymer backbone,
- (b) a melt flow ratio, $I_{10}/I_2 \geq 5.63$, and
- (c) a molecular weight distribution, M_w/M_n from 1.5 to 2.5.

The elastic substantially linear olefin polymers also have a processing index (PI) less than or equal to about 70 percent of the PI of a comparative linear olefin polymer at about the same I_2 and M_w/M_n .

Compositions comprising the substantially linear olefin polymer and at least one other natural or synthetic polymer are also within the scope of the invention.

Elastic substantially linear olefin polymers comprising ethylene homopolymers or an interpolymer of ethylene with at least one C₃-C₂₀ α -olefin copolymers are especially preferred.

Brief Description of the Drawings

Figure 1 is a schematic representation of a polymerization process suitable for making the polymers of the present invention.

Figure 2 plots data describing the relationship between I_{10}/I_2 and M_w/M_n for two examples of the invention, and for some comparative examples.

Figure 3 plots the shear stress versus shear rate for an example of the invention and for a comparative example, described herein.

Figure 4 plots the shear stress versus shear rate for an example of the invention and for a comparative example, described herein.

Figure 5 plots the heat seal strength versus heat seal temperature of film made from examples of the invention, and for comparative examples, described herein.

Figure 6 graphically displays dynamic shear viscosity data for an elastic substantially linear olefin polymer of the present invention and for a comparative linear polymer made using single site catalyst technology.

Figure 7 graphically displays I_{10}/I_2 ratio as a function of ethylene concentration in the polymerization reactor for ethylene/propene substantially linear copolymers of the invention.

Detailed Description of the Invention

The term "linear olefin polymers" used herein means that the olefin polymer does not have long chain branching. That is, the linear olefin polymer has an absence of long chain branching, as for example the traditional linear low density polyethylene polymers or linear high density polyethylene polymers made using Ziegler polymerization processes (e.g., US-A-4,076,698 (Anderson et al.)), sometimes called heterogeneous polymers. The term "linear olefin polymers" does not refer to high pressure branched polyethylene, ethylene/vinyl acetate copolymers, or ethylene/vinyl alcohol copolymers which are known to those skilled in the art to have numerous long chain branches. The term "linear olefin polymers" also refers to polymers made using uniform branching distribution polymerization processes, sometimes called homogeneous polymers. Such uniformly branched or homogeneous polymers include those made as described in US-A-3,645,992 (Elston) and those made using so-called single site catalysts in a batch reactor having relatively high olefin concentrations (as described in U.S.-A-5,026,798 (Canich) or in U.S.-A-5,055,438 (Canich)) or those made using constrained geometry catalysts in a batch reactor also having relatively high olefin concentrations (as described in US-A-5,064,802 (Stevens et al.) or in EP-A-0 416 815 (Stevens et al.)). The uniformly branched/homogeneous polymers are those polymers in which the comonomer is randomly distributed within a given interpolymer molecule and wherein substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer, but these polymers too have an absence of long chain branching, as, for example, Exxon Chemical has taught in their February 1992 Tappi Journal paper.

The term "substantially linear" polymers means that the polymer backbone is substituted with 0.01 long chain branches/1000 carbons to 3 long chain branches/1000 carbons, more preferably from 0.01 long chain branches/1000 carbons to 1 long chain branches/1000 carbons, and especially from 0.05 long chain branches/1000 carbons to 1 long chain branches/1000 carbons. Similar to the traditional homogeneous polymers, the substantially linear ethylene/ α -olefin copolymers of the invention have only a single melting point, as opposed to traditional Ziegler polymerized heterogeneous linear ethylene/ α -olefin copolymers which have two or more melting points (determined using differential scanning calorimetry (DSC)).

Long chain branching is defined herein as a chain length of at least about 6 carbons, above which the length cannot be distinguished using ^{13}C nuclear magnetic resonance spectroscopy. The long chain branch can be as long as about the same length as the length of the polymer backbone.

Long chain branching is determined by using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and is quantified using the method of Randall (*Rev. Macromol. Chem. Phys.*, C29 (2&3), p. 285-297), the disclosure of which is incorporated herein by reference.

"Melt tension" is measured by a specially designed pulley transducer in conjunction with the melt indexer. Melt tension is the load that the extrudate or filament exerts while passing over the pulley at the standard speed of 30 rpm. The melt tension measurement is similar to the "Melt Tension Tester" made by Toyoseiki and is described by John Dealy in "Rheometers for Molten Plastics", published by Van Nostrand Reinhold Co. (1982) on page 250-251. The melt tension of these new polymers is also surprisingly good, e.g., as high as about 2 grams or more, especially for the substantially linear olefin polymers which have a very narrow molecular weight distribution (i.e., M_w/M_n from 1.5 to 2.5).

The SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, in Wild et al, *Journal of Polymer Science, Poly. Phys. Ed.*, Vol. 20, p. 441 (1982), or as described in US-A-4,798,081. The SCBDI or CDBI for the substantially linear olefin polymers of the present invention is preferably greater than about 30 percent, especially greater than about 50 percent.

A unique characteristic of the presently claimed polymers is a highly unexpected flow property where the I_{10}/I_2 value is essentially independent of polydispersity index (i.e. M_w/M_n). This is contrasted with conventional Ziegler polymerized heterogeneous polyethylene resins and with conventional single site catalyst polymerized homogeneous polyethylene resins having rheological properties such that as the polydispersity index increases, the I_{10}/I_2 value also increases.

The density of the ethylene or ethylene/ α -olefin substantially linear olefin polymers in the present invention is measured in accordance with ASTM D-792 and is generally from 0.85 g/cm³ to 0.97 g/cm³, preferably from 0.85 g/cm³ to 0.955 g/cm³, and especially from 0.85 g/cm³ to 0.92 g/cm³.

The molecular weight of the ethylene or ethylene/ α -olefin substantially linear olefin polymers in the present invention is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/2.16 kg (formally known as "Condition (E)" and also known as 12). Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. The melt index for the ethylene or ethylene/ α -olefin substantially linear olefin polymers used herein is generally from 0.01 grams/10 minutes (g/10 min) to 1000 g/10 min, preferably from 0.01 g/10 min to 100 g/10 min, and especially from 0.01 g/10 min to 10 g/10 min.

Another measurement useful in characterizing the molecular weight of the substantially linear olefin polymers is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/10 kg (formerly known as "Condition (N)" and also known as I_{10}). The ratio of these two melt index terms is the melt flow ratio and is designated as I_{10}/I_2 . For the substantially linear ethylene/ α -olefin polymers of the invention, the I_{10}/I_2 ratio indicates the degree of long chain branching, i.e., the higher the I_{10}/I_2 ratio, the more long chain branching in the polymer. Generally, the I_{10}/I_2 ratio of the substantially linear ethylene/ α -olefin polymers is at least about 5.63, preferably at least about 7, especially at least about 8 or above.

Additives such as antioxidants (e.g., hindered phenolics (e.g., Irganox® 1010 made by Ciba Geigy Corp.), phosphites (e.g., Irgafos® 168 made by Ciba Geigy Corp.)), cling additives (e.g., PIB), antiblock additives, pigments, and the like can also be included in the polyethylene compositions, to the extent that they do not interfere with the enhanced properties of the polyolefins of the invention.

Molecular Weight Distribution Determination

The whole interpolymer product samples and the individual interpolymer samples are analyzed by gel permeation chromatography (GPC) on a Waters 150C high temperature chromatographic unit equipped with three mixed porosity columns (Polymer Laboratories 10³, 10⁴, 10⁵, and 10⁶), operating at a system temperature of 140°C. The solvent is

1,2,4-trichlorobenzene, from which 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is 1.0 milliliters/minute and the injection size is 200 microliters.

The molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Word in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968) to derive the following equation:

$$M_{\text{polyethylene}} = a \cdot (M_{\text{polystyrene}})^b$$

In this equation, $a = 0.4316$ and $b = 1.0$. Weight average molecular weight, M_w , is calculated in the usual manner according to the following formula: $M_w = \sum w_i \cdot M_i$, where w_i and M_i are the weight fraction and molecular weight, respectively, of the i^{th} fraction eluting from the GPC column.

The molecular weight distribution (M_w/M_n) for the substantially linear olefin polymers of the invention is generally less than 5, preferably from 1.5 to 2.5, and especially from 1.7 to 2.3.

Processing Index Determination

The rheological processing index (PI) is measured by a gas extrusion rheometer (GER). The GER is described by M. Shida, R.N. Shroff and L.V. Cancio in *Polym. Eng. Sci.*, Vol. 17, no. 11, p. 770 (1977), and in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on page 97-99. The processing index is measured at a temperature of 190°C, at nitrogen pressure of 17.2×10^6 N/m² gauge (2500 psig) using a 752 micrometers (0.0296 inch) diameter, 20:1 L/D die having an entrance angle of 180°. The GER processing index is calculated in millipoise units from the following equation:

$$PI = 21.5 \text{ N/cm}^2 (2.15 \times 10^6 \text{ dynes/cm}^2) / (1000 \times \text{shear rate}),$$

where:

21.5 N/cm² (2.15×10^6 dynes/cm²) is the shear stress at 17.2×10^6 N/m² (2500 psi), and the shear rate is the shear rate at the wall as represented by the following equation:

$$32 Q' / (60 \text{ sec/min})(0.745)(\text{Diameter} \times 2.54 \text{ cm/in})^3,$$

where:

Q' is the extrusion rate (gms/min),

0.745 is the melt density of polyethylene (gm/cm³), and

Diameter is the orifice diameter of the capillary (inches).

The PI is the apparent viscosity of a material measured at apparent shear stress of 21.5 N/cm² (2.15×10^6 dyne/cm²).

For the substantially linear olefin polymers disclosed herein, the PI is less than or equal to 70 percent of that of a comparative linear olefin polymer at about the same I_2 and M_w/M_n .

An apparent shear stress vs. apparent shear rate plot is used to identify the melt fracture phenomena. According to Ramamurthy in Journal of Rheology, 30(2), 337-357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular gloss to the more severe form of "sharkskin". In this disclosure, the onset of surface melt fracture is characterized at the beginning of losing extrudate gloss at which the surface roughness of extrudate can only be detected by 40X magnification. The critical shear rate at onset of surface melt fracture for the substantially linear olefin polymers is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n . Preferably, the critical shear stress at onset of surface melt fracture for the substantially linear olefin polymers of the invention is greater than 28 N/cm² (2.8×10^6 dynes/cm²).

Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (e.g., in blown film products), surface defects

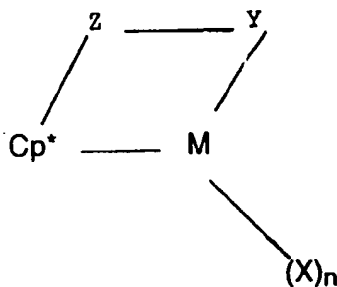
should be minimal, if not absent. The critical shear rate at onset of surface melt fracture (OSMF) and critical shear stress at onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER. For the substantially linear olefin polymers of the invention, the critical shear stress at onset of gross melt fracture is preferably greater than 40 N/cm² (4×10^6 dynes/cm²).

The Constrained Geometry Catalyst

Suitable constrained geometry catalysts for use herein preferably include constrained geometry catalysts as disclosed in EP-A-0 416 815. The monocyclopentadienyl transition metal olefin polymerization catalysts taught in US-A-5,026,798, are also believed to be suitable for use in preparing the polymers of the present invention, so long as the polymerization conditions substantially conform to those.

The foregoing catalysts may be further described as comprising a metal coordination complex comprising a metal of groups 3-10 or the Lanthanide series of the Periodic Table of the Elements and a delocalized π -bonded moiety substituted with a constrain-inducing moiety, said complex having a constrained geometry about the metal atom such that the angle at the metal between the centroid of the delocalized, substituted π -bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar π -bonded moiety lacking in such constrain-inducing substituent, and provided further that for such complexes comprising more than one delocalized, substituted π -bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted π -bonded moiety. The catalyst further comprises an activating cocatalyst.

Preferred catalyst complexes correspond to the formula:



wherein:

M is a metal of group 3-10, or the Lanthanide series of the Periodic Table of the Elements;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

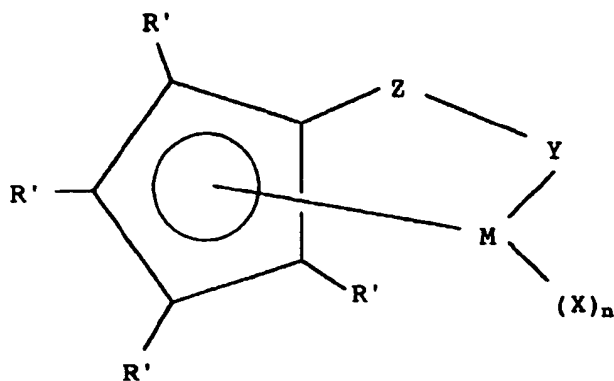
Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

Y is an anionic or nonanionic ligand group bonded to Z and M comprising nitrogen, phosphorus, oxygen or sulfur and having up to 20 non-hydrogen atoms, optionally Y and Z together form a fused ring system.

More preferably still, such complexes correspond to the formula:



wherein:

R' each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, germlyl, cyano, halo and combinations thereof having up to 20 non-hydrogen atoms;

X each occurrence independently is selected from the group consisting of hydride, halo, alkyl, aryl, silyl, germlyl, aryloxy, alkoxy, amide, siloxy, neutral Lewis base ligands and combinations thereof having up to 20 non-hydrogen atoms;

Y is -O-, -S-, -NR*, -PR*, or a neutral two electron donor ligand selected from the group consisting of OR*, SR*, NR*₂ or PR*₂;

M is as previously defined; and

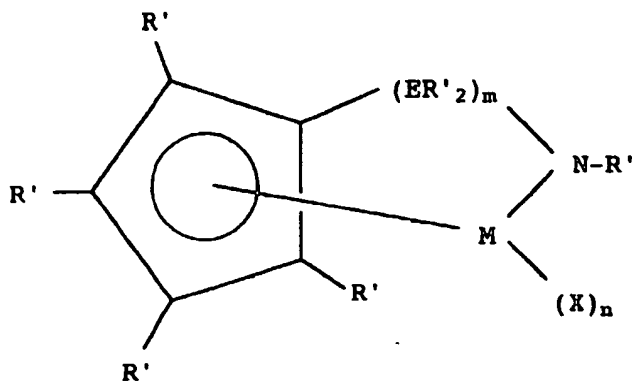
Z is SiR*₂, CR*₂, SiR*₂SiR*₂, CR*₂CR*₂, CR*=CR*, CR*₂SiR*₂, GeR*₂, BR*, BR*₂; wherein

R* each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 non-hydrogen atoms, and mixtures thereof, or two or more R* groups from Y, Z, or both Y and Z form a fused ring system; and n is 1 or 2.

It should be noted that whereas formula I and the following formulas indicate a cyclic structure for the catalysts, when Y is a neutral two electron donor ligand, the bond between M and Y is more accurately referred to as a coordinate-covalent bond. Also, it should be noted that the complex may exist as a dimer or higher oligomer.

Further preferably, at least one of R', Z, or R* is an electron donating moiety. Thus, highly preferably Y is a nitrogen or phosphorus containing group corresponding to the formula -N(R*)- or -P(R*)-, wherein R* is C₁₋₁₀ alkyl or aryl, i.e., an amido or phosphido group.

Most highly preferred complex compounds are amidosilane- or amidoalkanediy- compounds corresponding to the formula:



wherein:

M is titanium, zirconium or hafnium, bound in an η^5 bonding mode to the cyclopentadienyl group;

R' each occurrence is independently selected from the group consisting of hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

E is silicon or carbon;

X independently each occurrence is hydride, halo, alkyl, aryl, aryloxy or alkoxy of up to 10 carbons;

m is 1 or 2; and

n is 1 or 2.

Examples of the above most highly preferred metal coordination compounds include compounds wherein the R' on the amido group is methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; the cyclopentadienyl group is cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl, etc.; R' on the foregoing cyclopentadienyl groups each occurrence is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; and X is chloro, bromo, iodo, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc. Specific compounds include: (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (ethylamido)(tetramethyl- η^5 -cyclopentadienyl)-methylene titanium dichloride, (tertbutylamido)dibenzyl(tetramethyl- η^5 -cyclopentadienyl) silanezirconium dibenzyl, (benzylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride, (phenylphosphido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanezirconium dibenzyl, (tertbutylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium dimethyl.

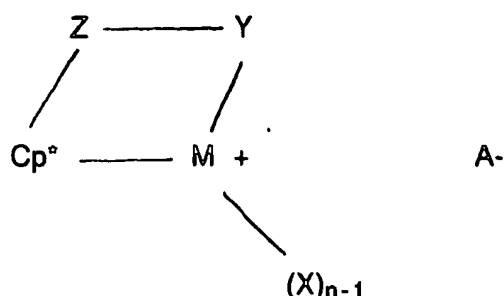
The complexes may be prepared by contacting a derivative of a metal, M, and a group I metal derivative or Grignard derivative of the cyclopentadienyl compound in a solvent and separating the salt byproduct. Suitable solvents for use in preparing the metal complexes are aliphatic or aromatic liquids such as cyclohexane, methylcyclohexane, pentane, hexane, heptane, tetrahydrofuran, diethyl ether, benzene, toluene, xylene, ethylbenzene, etc., or mixtures thereof.

In a preferred embodiment, the metal compound is MX_{n+1} , i.e., M is in a lower oxidation state than in the corresponding compound, MX_{n+2} and the oxidation state of M in the desired final complex. A noninterfering oxidizing agent may thereafter be employed to raise the oxidation state of the metal. The oxidation is accomplished merely by contacting the reactants utilizing solvents and reaction conditions used in the preparation of the complex itself. By the term "non-interfering oxidizing agent" is meant a compound having an oxidation potential sufficient to raise the metal oxidation state without interfering with the desired complex formation or subsequent polymerization processes. A particularly suitable noninterfering oxidizing agent is AgCl or an organic halide such as methylene chloride. The foregoing techniques are disclosed in EP-A-0 416 815 and EP-A-0 514 828.

Suitable cocatalysts for use herein include polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. So-called modified methyl aluminoxane (MMAO)

is also suitable for use as a cocatalyst. One technique for preparing such modified aluminoxane is disclosed in U.S.-A-5,041,584. Aluminoxanes can also be made as disclosed in U.S. Patents Nos. 5,542,199; 4,544,762; 5,015,749; and 5,041,585. Preferred cocatalysts are inert, noncoordinating, boron compounds.

Ionic active catalyst species which can be used to polymerize the polymers described herein correspond to the formula:



wherein:

M is a metal of group 3-10, or the Lanthanide series of the Periodic Table of the Elements;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

A- is a noncoordinating, compatible anion.

One method of making the ionic catalyst species which can be utilized to make the polymers of the present invention involve combining:

a) at least one first component which is a mono(cyclopentadienyl) derivative of a metal of Group 3-10 or the Lanthanide Series of the Periodic Table of the Elements containing at least one substituent which will combine with the cation of a second component (described hereinafter) which first component is capable of forming a cation formally having a coordination number that is one less than its valence, and

b) at least one second component which is a salt of a Bronsted acid and a noncoordinating, compatible anion.

More particularly, the non-coordinating, compatible anion of the Bronsted acid salt may comprise a single coordination complex comprising a charge-bearing metal or metalloid core, which anion is both bulky and non-nucleophilic. The recitation "metalloid", as used herein, includes non-metals such as boron, phosphorus and the like which exhibit semi-metallic characteristics.

Illustrative, but not limiting examples of monocyclopentadienyl metal components (first components) which may be used in the preparation of cationic complexes are derivatives of titanium, zirconium, vanadium, hafnium, chromium, lanthanum, etc. Preferred components are titanium or zirconium compounds. Examples of suitable monocyclopentadienyl metal compounds are hydrocarbyl-substituted monocyclopentadienyl metal compounds such as (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediylzirconium dimethyl, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium dimethyl, (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediylzirconium dibenzyl, (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium dimethyl, (ethylamido)(tetramethyl- η^5 -cyclopentadienyl)methylenetitanium dimethyl, (tertbutylamido)dibenzyl(tetramethyl- η^5 -cyclopentadienyl) silanezirconium dibenzyl, (benzylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium diphenyl, (phenylphosphido)

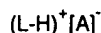
dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanezirconium dibenzyl.

Such components are readily prepared by combining the corresponding metal chloride with a dilithium salt of the substituted cyclopentadienyl group such as a cyclopentadienyl-alkanedyl, cyclopentadienyl-silane amide, or cyclopentadienyl-phosphide compound. The reaction is conducted in an inert liquid such as tetrahydrofuran, C₅₋₁₀ alkanes, toluene, etc. utilizing conventional synthetic procedures. Additionally, the first components may be prepared by reaction of a group II derivative of the cyclopentadienyl compound in a solvent and separating the salt by-product. Magnesium derivatives of the cyclopentadienyl compounds are preferred. The reaction may be conducted in an inert solvent such as cyclohexane, pentane, tetrahydrofuran, diethyl ether, benzene, toluene, or mixtures of the like. The resulting metal cyclopentadienyl halide complexes may be alkylated using a variety of techniques. Generally, the metal cyclopentadienyl alkyl or aryl complexes may be prepared by alkylation of the metal cyclopentadienyl halide complexes with alkyl or aryl derivatives of group I or group II metals. Preferred alkylating agents are alkyl lithium and Grignard derivatives using conventional synthetic techniques. The reaction may be conducted in an inert solvent such as cyclohexane, pentane, tetrahydrofuran, diethyl ether, benzene, toluene, or mixtures of the like.

A preferred solvent is a mixture of toluene and tetrahydrofuran.

Compounds useful as a second component in the preparation of the ionic catalysts useful in this invention will comprise a cation, which is a Bronsted acid capable of donating a proton, and a compatible noncoordinating anion. Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 3-10 or Lanthanide Series cation) which is formed when the two components are combined and sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers, nitriles and the like. Suitable metals, then, include, but are not limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially. In light of this, salts containing anions comprising a coordination complex containing a single boron atom are preferred.

Highly preferably, the second component useful in the preparation of the catalysts of this invention may be represented by the following general formula:



wherein:

L is a neutral Lewis base;

(L-H)⁺ is a Bronsted acid; and

[A]⁻ is a compatible, noncoordinating anion.

More preferably [A]⁻ corresponds to the formula:

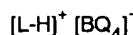


wherein:

M' is a metal or metalloid selected from Groups 5-15 of the Periodic Table of the Elements; and

Q independently each occurrence is selected from the Group consisting of hydride, dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, and substituted-hydrocarbyl radicals of up to 20 carbons with the proviso that in not more than one occurrence is Q halide and q is one more than the valence of M'.

Second components comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:



wherein:

L is a neutral Lewis base;

[L-H]⁺ is a Bronsted acid;

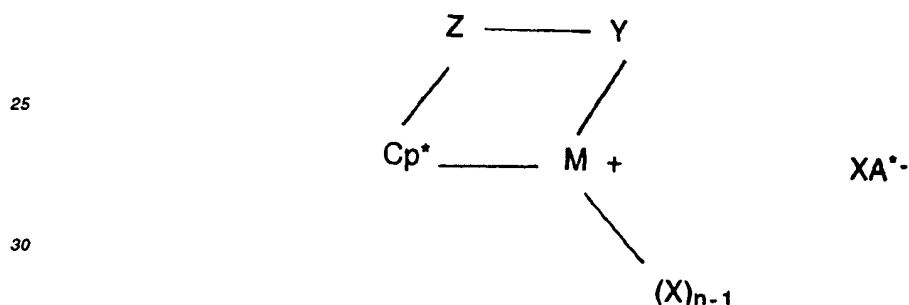
5 B is boron in a valence state of 3; and

Q is as previously defined.

10 Illustrative, but not limiting, examples of boron compounds which may be used as a second component in the preparation of the improved catalysts of this invention are trialkyl-substituted ammonium salts such as triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tris(n-butyl)ammonium tetraphenylborate, trimethylammonium tetrakis(p-tolyl)borate, tributylammonium tetrakis(pentafluorophenyl)borate, tripropylammonium tetrakis(2,4-dimethylphenyl)borate, tributylammonium tetrakis(3,5-dimethylphenyl)borate, triethylammonium tetrakis(3,5-ditri-
15 fluoromethylphenyl)borate and the like. Also suitable are N,N-dialkyl anilinium salts such as N,N-dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate, N,N-2,4,6-pentamethylanilinium tetraphenylborate and the like; dialkylammonium salts such as di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate, dicyclohexylammonium tetraphenylborate and the like; and triaryl phosphonium salts such as triphenylphosphonium tetraphenylborate, tri(methylphenyl)phosphonium tetrakis(pentafluorophenyl)borate, tri(dimethylphenyl)phosphonium tetraphenylborate.

Preferred ionic catalysts are those having a limiting charge separated structure corresponding to the formula:

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wherein

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M is a metal of group 3-10, or the Lanthanide series of the Periodic Table of the Elements;

Cp^{*} is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η⁵ bonding mode to M;

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Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp^{*} and Z together form a fused ring system;

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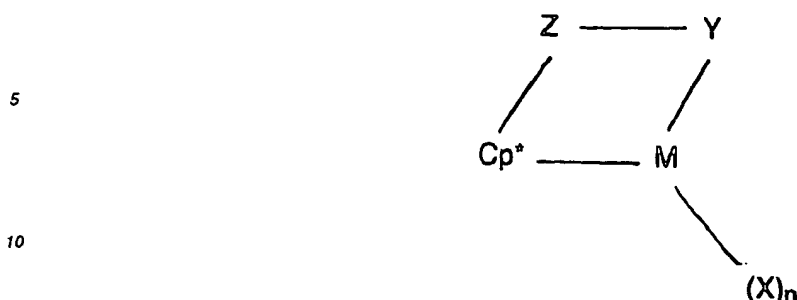
X independently each occurrence is an anionic ligand group or neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

50 XA^{•-} is -XB(C₆F₅)₃.

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This class of cationic complexes may be conveniently prepared by contacting a metal compound corresponding to the formula:



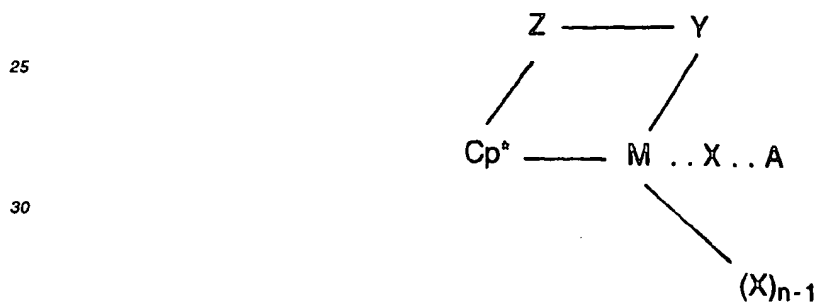
wherein:

15 Cp*, M, and n are as previously defined, with tris(pentafluorophenyl)borane cocatalyst under conditions to cause abstraction of X and formation of the anion $\text{XB}(\text{C}_6\text{F}_5)_3$.

Preferably X in the foregoing ionic catalyst is $\text{C}_1\text{-C}_{10}$ hydrocarbyl, most preferably methyl.

The preceding formula is referred to as the limiting, charge separated structure. However, it is to be understood that, particularly in solid form, the catalyst may not be fully charge separated. That is, the X group may retain a partial covalent bond to the metal atom, M. Thus, the catalysts may be alternately depicted as possessing the formula:

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35 The catalysts are preferably prepared by contacting the derivative of a Group 4 or Lanthanide metal with the tris (pentafluorophenyl)borane in an inert diluent such as an organic liquid. Tris(pentafluorophenyl)borane is a commonly available Lewis acid that may be readily prepared according to known techniques. The compound is disclosed in Marks, et al. *J. Am. Chem. Soc.*, 1991, 113, 3623-3625 for use in alkyl abstraction of zirconocenes.

40 All reference to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

It is believed that in the constrained geometry catalysts used herein the metal atom is forced to greater exposure of the active metal site because one or more substituents on the single cyclopentadienyl or substituted metal is both bonded to an adjacent covalent moiety and held in association with the cyclopentadienyl group through an η^5 or other π -bonding interaction. It is understood that each respective bond between the metal atom and the constituent atoms of the cyclopentadienyl or substituted cyclopentadienyl group need not be equivalent. That is, the metal may be symmetrically or unsymmetrically π -bound to the cyclopentadienyl or substituted cyclopentadienyl group.

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The geometry of the active metal site is further defined as follows. The centroid of the cyclopentadienyl or substituted cyclopentadienyl group may be defined as the average of the respective X, Y, and Z coordinates of the atomic centers forming the cyclopentadienyl or substituted cyclopentadienyl group. The angle, Θ , formed at the metal center between the centroid of the cyclopentadienyl or substituted cyclopentadienyl group and each other ligand of the metal complex may be easily calculated by standard techniques of single crystal X-ray diffraction. Each of these angles may increase or decrease depending on the molecular structure of the constrained geometry metal complex. Those complexes wherein one or more of the angles, Θ , is less than in a similar, comparative complex differing only in the fact that the constrain inducing substituent is replaced by hydrogen, have constrained geometry for purposes of the present invention. Preferably one or more of the above angles, Θ , decrease by at least 5 percent, more preferably 7.5 percent, compared to the comparative complex. Highly preferably, the average value of all bond angles, Θ , is also less than in the comparative complex.

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Preferably, monocyclopentadienyl metal coordination complexes of group 4 or lanthanide metals according to the present invention have constrained geometry such that the smallest angle, Θ , between the centroid of the Cp* group and the Y substituent, is less than 115° , more preferably less than 110° , most preferably less than 105° , and especially less than 100° .

Other compounds which are useful in the catalyst compositions of this invention, specially compounds containing other Group 4 or Lanthanide metals, will, of course, be apparent to those skilled in the art.

Polymerization

The improved melt elasticity and processibility of the substantially linear polymers according to the present invention result, it is believed, from their method of production. The polymers may be produced via a continuous (as opposed to a batch) controlled polymerization process using at least one reactor, but can also be produced using multiple reactors (e.g., using a multiple reactor configuration as described in US-A-3,914,342) at a polymerization temperature and pressure sufficient to produce the interpolymers having the desired properties.

In polymerizing ethylene and ethylene/ α -olefin copolymers, a batch reactor process typically operates at an ethylene concentration from about 6.7 to about 12.5 percent by weight of the reactor contents and have a polymer concentration generally less than about 5 percent by weight of the reactor contents, dependent upon the ethylene solubility, which is a function of reactor temperature and pressure.

According to one embodiment of the present process, the polymers are produced in a continuous process, as opposed to a batch process. Preferably, the polymerization temperature of the continuous process is from about 20°C to about 250°C , using constrained geometry catalyst technology. If a narrow molecular weight distribution polymer (M_w/M_n of from about 1.5 to about 2.5) having a higher I_0/I_2 ratio (e.g. I_0/I_2 of 7 or more, preferably at least 8, especially at least 9) is desired, the ethylene concentration in the reactor is preferably not more than about 8 percent by weight of the reactor contents, especially not more than about 6 percent by weight of the reactor contents, and most especially not more than about 4 percent by weight of the reactor contents. Preferably, the polymerization is performed in a solution polymerization process. Generally, manipulation of I_0/I_2 while holding M_w/M_n relatively low for producing the novel polymers described herein is a function of reactor temperature and/or ethylene concentration. Reduced ethylene concentration and higher temperature generally produces higher I_0/I_2 . Generally, as the ethylene concentration of the reactor decreases, the polymer concentration increases. For the novel substantially linear ethylene/ α -olefin copolymers and substantially linear ethylene homopolymers claimed herein, the polymer concentration for a continuous solution polymerization process is preferably above about 5 weight percent of the reactor contents, especially above about 6 weight percent of the reactor contents.

When using olefins other than ethylene as the primary monomer, suitable adjustments can be made regarding polymerization temperature, pressure and olefin concentration, depending on the olefin to be polymerized or copolymerized, but generally the olefin concentration is less than that normally useful in a batch reactor and the polymer concentration is higher than that normally useful in a batch reactor.

The substantially linear polymers of the present invention can be homopolymers of $\text{C}_2\text{-C}_{20}$ α -olefins, such as ethylene, propylene, 4-methyl-1-pentene, etc., or they can be interpolymers of ethylene with at least one $\text{C}_3\text{-C}_{20}$ α -olefin and/or $\text{C}_2\text{-C}_{20}$ acetylenically unsaturated monomer and/or $\text{C}_4\text{-C}_{18}$ diolefins. The substantially linear polymers of the present invention can also be interpolymers of ethylene with at least one of the above $\text{C}_3\text{-C}_{20}$ α -olefins, diolefins and/or acetylenically unsaturated monomers in combination with other unsaturated monomers.

Monomers usefully polymerized according to the present invention include, for example, ethylenically unsaturated monomers, acetylenic compounds, conjugated or nonconjugated dienes, polyenes, carbon monoxide, etc. Preferred monomers include the $\text{C}_2\text{-C}_{10}$ α -olefins especially ethylene, 1-propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene, halo- or alkyl substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutane, 1,4-hexadiene, and naphthenics (e.g., cyclopentene, cyclohexene and cyclooctene).

Other unsaturated monomers usefully polymerized according to the present invention include, for example, ethylenically unsaturated monomers, conjugated or nonconjugated dienes, polyenes, etc. Preferred monomers include the $\text{C}_2\text{-C}_{10}$ α -olefins especially ethylene, propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene, halo- or alkyl substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutane, 1,4-hexadiene, and naphthenics (e.g., cyclopentene, cyclohexene and cyclooctene).

The polymerization conditions for manufacturing the polymers of the present invention are generally those useful in the solution polymerization process, although the application of the present invention is not limited thereto. Slurry and gas phase polymerization processes are also believed to be useful, provided the proper catalysts and polymerization conditions are employed.

Multiple reactor polymerization processes are also useful in the present invention, such as those disclosed in US-A-3,914,342. The multiple reactors can be operated in series or in parallel, with one constrained geometry catalyst

employed in at least one of the reactors.

In general, the continuous polymerization according to the present invention may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0 to 250°C and pressures from atmospheric to 1000 atmospheres (100 MPa). Suspension, solution, slurry, gas phase or other process conditions may be employed if desired. A support may be employed but preferably the catalysts are used in a homogeneous (i.e., soluble) manner. It will, of course, be appreciated that the active catalyst system, especially nonionic catalysts, form *in situ* if the catalyst and the cocatalyst components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to form the active catalyst in a separate step in a suitable solvent prior to adding the same to the polymerization mixture.

The polymerization conditions for manufacturing the polymers of the present invention are generally those useful in the solution polymerization process, although the application of the present invention is not limited thereto. Gas phase polymerization processes are also believed to be useful, provided the proper catalysts and polymerization conditions are employed.

Fabricated articles made from the novel olefin polymers may be prepared using all of the conventional polyolefin processing techniques. Useful articles include films (e.g., cast, blown and extrusion coated), fibers (e.g., staple fibers (including use of a novel olefin polymer disclosed herein as at least one component comprising at least a portion of the fiber's surface), spunbond fibers or melt blown fibers (using, e.g., systems as disclosed in US-A-4,340,563, US-A-4,663,220, US-A-4,668,566, or US-A-4,322,027), and gel spun fibers (e.g., the system disclosed in US-A-4,413,110)), both woven and nonwoven fabrics (e.g., spunlaced fabrics disclosed in US-A-3,485,706) or structures made from such fibers (including, e.g., blends of these fibers with other fibers, e.g., PET or cotton) and molded articles (e.g., made using an injection molding process, a blow molding process or a rotomolding process). The new polymers described herein are also useful for wire and cable coating operations, impact modification, especially at low temperatures, of thermoplastic olefins (e.g., polypropylene), as well as in sheet extrusion for vacuum forming operations.

Useful compositions are also suitably prepared comprising the substantially linear polymers of the present invention and at least one other natural or synthetic polymer. Preferred other polymers include thermoplastics such as styrene-butadiene block copolymers, polystyrene (including high impact polystyrene), ethylene vinyl alcohol copolymers, ethylene acrylic acid copolymers, other olefin copolymers (especially polyethylene copolymers) and homopolymers (e.g., those made using conventional heterogeneous catalysts). Examples include polymers made by the process of US-A-4,076,698, other linear or substantially linear polymers of the present invention, and mixtures thereof. Other substantially linear polymers of the present invention and conventional HDPE and/or LLDPE are preferred for use in the thermoplastic compositions.

The compositions comprising the substantially linear olefin polymers are formed by any convenient method, including dry blending the individual components and subsequently melt mixing, either directly in the extruder used to make the finished article (e.g., film), or by pre-melt mixing in a separate extruder. The polyethylene compositions may also be prepared by multiple reactor polymerization techniques. For example, one reactor may polymerize the constrained geometry catalyzed polyethylene and another reactor polymerize the heterogeneous catalyzed polyethylene, either in series or in parallel operation.

Compositions comprising the olefin polymers can also be formed into fabricated articles such as those previously mentioned using conventional polyolefin processing techniques which are well known to those skilled in the art of polyolefin processing.

For examples described herein, unless otherwise stipulated, all procedures were performed under an inert atmosphere of nitrogen or argon. Solvent choices were often optional, for example, in most cases either pentane or 30-60 petroleum ether can be interchanged. Amines, silanes, lithium reagents, and Grignard reagents were purchased from Aldrich Chemical Company. Published methods for preparing tetramethylcyclopentadiene ($C_5Me_4H_2$) and lithium tetramethylcyclopentadienide ($Li(C_5Me_4H)$) include C. M. Fendrick et al. *Organometallics*, 3, 819 (1984). Lithiated substituted cyclopentadienyl compounds may be typically prepared from the corresponding cyclopentadiene and a lithium reagent such as n-butyl lithium. Titanium trichloride ($TiCl_3$) was purchased from Aldrich Chemical Company. The tetrahydrofuran adduct of titanium trichloride, $TiCl_3(THF)_3$, was prepared by refluxing $TiCl_3$ in THF overnight, cooling, and isolating the blue solid product, according to the procedure of L. E. Manzer, *Inorg. Syn.*, 21, 135 (1982).

Examples 1-4

The metal complex solution for Example 1 is prepared as follows:

Part 1: Prep of $Li(C_5Me_4H)$

In the drybox, a 3L 3-necked flask was charged with 18.34 g of $C_5Me_4H_2$, 800 mL of pentane, and 500 mL of ether.

The flask was topped with a reflux condenser, a mechanical stirrer, and a constant addition funnel containing 63 mL of 2.5 M n-BuLi in hexane. The BuLi was added dropwise over several hours. A very thick precipitate formed; approx. 1000 mL of additional pentane had to be added over the course of the reaction to allow stirring to continue. After the addition was complete, the mixture was stirred overnight. The next day, the material was filtered, and the solid was thoroughly washed with pentane and then dried under reduced pressure. 14.89 g of $\text{Li}(\text{C}_5\text{Me}_4\text{H})$ was obtained (78 percent).

Part 2: Prep of $\text{C}_5\text{Me}_4\text{HSiMe}_2\text{Cl}$

In the drybox 30.0 g of $\text{Li}(\text{C}_5\text{Me}_4\text{H})$ was placed in a 500 mL Schlenk flask with 250 mL of THF and a large magnetic stir bar. A syringe was charged with 30 mL of Me_2SiCl_2 and the flask and syringe were removed from the drybox. On the Schlenk line under a flow of argon, the flask was cooled to -78°C , and the Me_2SiCl_2 added in one rapid addition. The reaction was allowed to slowly warm to room temperature and stirred overnight. The next morning the volatile materials were removed under reduced pressure, and the flask was taken into the drybox. The oily material was extracted with pentane, filtered, and the pentane was removed under reduced pressure to leave the $\text{C}_5\text{Me}_4\text{HSiMe}_2\text{Cl}$ as a clear yellow liquid (46.83 g; 92.9 percent).

Part 3: Prep of $\text{C}_5\text{Me}_4\text{HSiMe}_2\text{NH}^t\text{Bu}$

In the drybox, a 3-necked 2 L flask was charged with 37.4 g of t-butylamine and 210 mL of THF. $\text{C}_5\text{Me}_4\text{HSiMe}_2\text{Cl}$ (25.47 g) was slowly dripped into the solution over 3-4 hours. The solution turned cloudy and yellow. The mixture was stirred overnight and the volatile materials removed under reduced pressure. The residue was extracted with diethyl ether, the solution was filtered, and the ether removed under reduced pressure to leave the $\text{C}_5\text{Me}_4\text{HSiMe}_2\text{NH}^t\text{Bu}$ as a clear yellow liquid (26.96 g; 90.8 percent).

Part 4: Prep of $[\text{MgCl}]_2[\text{Me}_4\text{C}_5\text{SiMe}_2\text{N}^t\text{Bu}](\text{THF})_x$

In the drybox, 14.0 mL of 2.0 M isopropylmagnesium chloride in ether was syringed into a 250 mL flask. The ether was removed under reduced pressure to leave a colorless oil. 50 mL of a 4:1 (by volume) toluene:THF mixture was added followed by 3.50 g of $\text{Me}_4\text{HC}_5\text{SiMe}_2\text{NH}^t\text{Bu}$. The solution was heated to reflux. After refluxing for 2 days, the solution was cooled and the volatile materials removed under reduced pressure. The white solid residue was slurried in pentane and filtered to leave a white powder, which was washed with pentane and dried under reduced pressure. The white powder was identified as $[\text{MgCl}]_2[\text{Me}_4\text{C}_5\text{SiMe}_2\text{N}^t\text{Bu}](\text{THF})_x$ (yield: 6.7 g).

Part 5: Prep of $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{N}^t\text{Bu})]\text{TiCl}_2$

In the drybox, 0.50 g of $\text{TiCl}_3(\text{THF})_3$ was suspended in 10 mL of THF. 0.69 g of solid $[\text{MgCl}]_2[\text{Me}_4\text{C}_5\text{SiMe}_2\text{N}^t\text{Bu}](\text{THF})_x$ was added, resulting in a color change from pale blue to deep purple. After 15 minutes, 0.35 g of AgCl was added to the solution. The color immediately began to lighten to a pale green/yellow. After 1.5 hours, the THF was removed under reduced pressure to leave a yellow-green solid. Toluene (20 mL) was added, the solution was filtered, and the toluene was removed under reduced pressure to leave a yellow-green solid, 0.51 g (quantitative yield) identified by ^1H NMR as $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{N}^t\text{Bu})]\text{TiCl}_2$.

Part 6: Preparation of $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{N}^t\text{Bu})]\text{TiMe}_2$

In an inert atmosphere glove box, 9.031 g of $[\text{C}_5\text{Me}_4(\text{Me}_2\text{SiN}^t\text{Bu})]\text{TiCl}_2$ is charged into a 250 mL flask and dissolved into 100 mL of THF. This solution is cooled to about -25°C by placement in the glove box freezer for 15 minutes. To the cooled solution is added 35 mL of a 1.4 M MeMgBr solution in toluene/THF (75/25). The reaction mixture is stirred for 20 to 25 minutes followed by removal of the solvent under vacuum. The resulting solid is dried under vacuum for several hours.

The product is extracted with pentane (4x50 mL) and filtered. The filtrate is combined and the pentane removed under vacuum giving the catalyst as a straw yellow solid.

The metal complex, $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{N}^t\text{Bu})]\text{TiMe}_2$, solution for Examples 2 and 3 is prepared as follows:

In an inert atmosphere glove box 10.6769 g of a tetrahydrofuran adduct of titanium trichloride, $\text{TiCl}_3(\text{THF})_3$, is loaded into a 1 L flask and slurried into 300 mL of THF. To this slurry, at room temperature, is added 17.402 g of $[\text{MgCl}]_2[\text{N}^t\text{BuSiMe}_2\text{C}_5\text{Me}_4](\text{THF})_x$ as a solid. An additional 200 mL of THF is used to help wash this solid into the reaction flask. This addition resulted in an immediate reaction giving a deep purple solution. After stirring for 5 minutes 9.23 mL of a 1.56 M solution of CH_2Cl_2 in THF is added giving a quick color change to dark yellow. This stage of the reaction is

allowed to stir for about 20 to 30 minutes. Next, 61.8 ml of a 1.4 M MeMgBr solution in toluene/THF(75/25) is added via syringe. After about 20 to 30 minutes stirring time the solvent is removed under vacuum and the solid dried. The product is extracted with pentane (8x50ml) and filtered. The filtrate is combined and the pentane removed under vacuum giving the metal complex as a tan solid.

5 The metal complex, $[C_5Me_4(SiMe_2NtBu)]TiMe_2$, solution for Example 4 is prepared as follows:

In an inert atmosphere glove box 4.8108 g of $TiCl_3(thf)_3$ is placed in a 500 ml flask and slurried into 130 ml of THF. In a separate flask 8.000 g of $[MgCl]_2[N^iBuSiMe_2C_5Me_4](THF)_x$ is dissolved into 150 ml of THF. These flasks are removed from the glove box and attached to a vacuum line and the contents cooled to $-30^\circ C$. The THF solution of $[MgCl]_2[N^iBuSiMe_2C_5Me_4](THF)_x$ is transferred (over a 15 minute period) via cannula to the flask containing the $TiCl_3(THF)_3$ slurry. This reaction is allowed to stir for 1.5 hours over which time the temperature warmed to $0^\circ C$ and the solution color turned deep purple. The reaction mixture is cooled back to $-30^\circ C$ and 4.16 ml of a 1.56 M CH_2Cl_2 solution in THF is added. This stage of the reaction is stirred for an additional 1.5 hours and the temperature warmed to $-10^\circ C$. Next, the reaction mixture is again cooled to $-40^\circ C$ and 27.81 ml of a 1.4 M MeMgBr solution in toluene/THF (75/25) was added via syringe and the reaction is now allowed to warm slowly to room temperature over 3 hours. After this time the solvent is removed under vacuum and the solid dried. At this point the reaction flask is brought back into the glove box where the product is extracted with pentane (4x50 ml) and filtered. The filtrate is combined and the pentane removed under vacuum giving the catalyst as a tan solid. The metal complex is then dissolved into a mixture of C_8 - C_{10} saturated hydrocarbons (e.g., Isopar™ E, made by Exxon) and ready for use in polymerization.

20 Polymerization

The polymer products of Examples 1-4 are produced in a solution polymerization process using a continuously stirred reactor. Additives (e.g., antioxidants, pigments, etc.) can be incorporated into the interpolymer products either during the pelletization step or after manufacture, with a subsequent re-extrusion. Examples 1-4 are each stabilized with 1250 ppm Calcium Stearate, 200 ppm Irganox 1010, and 1600 ppm Irgafos 168. Irgafos™ 168 is a phosphite stabilizer and Irganox™ 1010 is a hindered polyphenol stabilizer (e.g., tetrakis [methylene 3-(3,5-ditert.butyl-4-hydroxyphenyl)propionate])methane. Both are trademarks of and made by Ciba-Geigy Corporation. A representative schematic for the polymerization process is shown in Figure 1.

The ethylene (4) and the hydrogen (5) are combined into one stream (15) before being introduced into the diluent mixture (3). Typically, the diluent mixture comprises a mixture of C_8 - C_{10} saturated hydrocarbons (1), (e.g., Isopar™ E, made by Exxon) and the comonomer(s) (2). For example 1, the comonomer is 1-octene. The reactor feed mixture (6) is continuously injected into the reactor (9). The metal complex (7) and the cocatalyst (8) (the cocatalyst is tris (pentafluorophenyl)borane for Examples 1-4 herein which forms the ionic catalyst in situ) are combined into a single stream and also continuously injected into the reactor. Sufficient residence time is allowed for the metal complex and cocatalyst to react to the desired extent for use in the polymerization reactions, at least about 10 seconds. For the polymerization reactions of Examples 1-4, the reactor pressure is held constant at about 3.4×10^6 N/m² gauge (490 psig). Ethylene content of the reactor, after reaching steady state, is maintained below about 8 percent.

After polymerization, the reactor exit stream (14) is introduced into a separator (10) where the molten polymer is separated from the unreacted comonomer(s), unreacted ethylene, unreacted hydrogen, and diluent mixture stream (13). The molten polymer is subsequently strand chopped or pelletized and, after being cooled in a water bath or pelletizer (11), the solid pellets are collected (12). Table 1 describes the polymerization conditions and the resultant polymer properties:

Table 1

Example	1	2	3	4
Ethylene feed rate kg/hr (lbs/hr)	1.45 (3.2)	1.72 (3.8)	1.72 (3.8)	1.72 (3.8)
Comonomer/Olefin* ratio (mole percent)	12.3	0	0	0
Hydrogen/ethylene ratio (mole percent)	0.054	0.072	0.083	0.019
Diluent/ethylene ratio (weight basis)	9.5	7.4	8.7	8.7
Metal complex conc. (molar)	0.00025	0.0005	0.001	0.001
Metal complex flow rate (ml/min)	5.9	1.7	2.4	4.8
Cocatalyst conc. (molar)	0.001	0.001	0.002	0.002

*For Examples 1-4, the Comonomer/Olefin ratio is defined as the percentage molar ratio of ((1-octene)/(1-octene + ethylene))

Table 1 (continued)

Example	1	2	3	4
Cocatalyst flow rate (ml/min)	2.9	1.3	6	11.9
Reactor temp (°C)	114	160	160	200
Ethylene conc. in the reactor exit stream (weight percent)	2.65	3.59	0.86	1.98
Product I ₂ (g/10 minutes)	1.22	0.96	1.18	0.25
Product density (g/cm ³)	0.903	0.954	0.954	0.953
Product I ₁₀ /I ₂	6.5	7.4	11.8	16.1
Product M _w /M _n	1.86	1.95	2.09	2.07

The ¹³C NMR spectrum of Example 3 (ethylene homopolymer) shows peaks which can be assigned to the αδ+, βδ+, and methine carbons associated with a long chain branch. Long chain branching is determined using the method of Randall described earlier in this disclosure, wherein he states that "Detection of these resonances in high-density polyethylenes where no 1-olefins were added during the polymerization should be strongly indicative of the presence of long chain branching." Using the equation 141 from Randall (p. 292):

$$\text{Branches per 10,000 carbons} = [((1/3)(\alpha)/T_{\text{Tot}})] \times 10^4,$$

wherein α= the average intensity of a carbon from a branch (αδ+) carbon and T_{Tot} = the total carbon intensity, the number of long chain branches in this sample is determined to be 3.4 per 10,000 carbon atoms, or 0.34 long chain branches/1000 carbon atoms.

Examples 5, 6 and Comparative Examples 7-9

Examples 5, 6 and comparison examples 7-9 with the same melt index are tested for rheology comparison. Examples 5 and 6 are the substantially linear polyethylenes produced by the constrained geometry catalyst technology, as described in Examples 1-4. Examples 5 and 6 are stabilized as Examples 1-4. Comparison examples 7, 8 and 9 are conventional heterogeneous Ziegler polymerization blown film resins Dowlex™ 2045A, Attane™ 4201, and Attane™ 4403, respectively, all of which are ethylene/1-octene copolymers made by The Dow Chemical Company.

Comparative example 7 is stabilized with 200 ppm Irganox™ 1010, and 1600 ppm Irgafos™ 168 while comparative examples 8 and 9 are stabilized with 200 ppm Irganox™ 1010 and 800 ppm PEPQ™. PEPQ™ is a trademark of Sandoz Chemical, the primary ingredient of which is believed to be tetrakis-(2,4-di-tertbutyl-phenyl)-4,4' biphenylphosphonite. A comparison of the physical properties of each example and comparative example is listed in Table 2.

Table 2

Property	Ex. 5	Ex. 6	Comparative example 7	Comparative example 8	Comparative example 9
I ₂ (g/10 minutes)	1	1	1	1	0.76
Density (g/cm ³)	0.92	0.902	0.92	0.912	0.905
I ₁₀ /I ₂	9.45	7.61	7.8 - 8	8.2	8.7
M _w /M _n	1.97	2.09	3.5 - 3.8	3.8	3.8 - 4

Surprisingly, even though the molecular weight distribution of Examples 5 and 6 is narrow (i.e., M_w/M_n is low), the I₁₀/I₂ values are higher in comparison with comparative examples 7-9. A comparison of the relationship between I₁₀/I₂ vs. M_w/M_n for some of the novel polymers described herein and conventional heterogeneous Ziegler polymers is given in Figure 2. The I₁₀/I₂ value for the novel polymers of the present invention is essentially independent of the molecular weight distribution, M_w/M_n which is not true for conventional Ziegler polymerized resins.

Example 5 and comparative example 7 with similar melt index and density (Table II) are also extruded via a Gas Extrusion Rheometer (GER) at 190°C using a 0.075 cm (0.0296") diameter, 20 UD die. The processing index (P.I.) is measured at an apparent shear stress of 21.5 N/cm² (2.15 x 10⁶ dyne/cm²) as described previously. The onset of gross

melt fracture can easily be identified from the shear stress vs. shear rate plot shown in Figure 3 where a sudden jump of shear rate occurs. A comparison of the shear stresses and corresponding shear rates before the onset of gross melt fracture is listed in Table 3. It is particularly interesting that the PI of Example 5 is more than 20 percent lower than the PI of comparative example 7 and that the onset of melt fracture or sharkskin for Example 5 is also at a significantly higher shear stress and shear rate in comparison with the comparative example 7. Furthermore, the Melt Tension (MT) as well as Elastic Modulus of Example 5 are higher than that of comparative example 7.

Table 3

Property	Example 5	Comparative example 7
I_2 (g/ 10 minutes)	1	1
I_{10}/I_2	9.45	7.8 - 8
PI (kpoise)	11	15
Melt tension (gms)	1.89	1.21
Elastic modulus at 0.1 rad/sec N/cm ² (dynes/cm ²)	(2425) 2.425×10^{-2}	(882.6) 8.826×10^{-3}
OGMF*, critical shear rate (1/sec)	> 1556 (not observed)	936
OGMF*, critical shear stress (MPa)	0.452	0.366
OSMF**, critical shear rate (1/sec)	> 1556 (not observed)	about 628
OSMF**, critical shear stress (MPa)	about 0.452	about 0.25

* Onset of Gross Melt Fracture.

** Onset of Surface Melt Fracture.

Example 6 and comparative example 9 have similar melt index and density, but example 6 has lower I_{10}/I_2 (Table 4). These polymers are extruded via a Gas Extrusion Rheometer (GER) at 190°C using a 0.075 cm (0.0296 inch) diameter, 20:1 UD die. The processing index (PI) is measured at an apparent shear stress of 21.5 N/cm² (2.15×10^6 dyne/cm²) as described previously.

Table 4

Property	Example 6	Comparative example 9
I_2 (g/ 10 minutes)	1	0.76
I_{10}/I_2	7.61	8.7
PI	(14 kpoise) 1400 N.sec/m ²	(15 kpoise) 1500 N.sec/m ²
Melt tension (gms)	1.46	1.39
Elastic modulus at 0.1 rad/sec N/cm ² (dynes/cm ²)	(1481) 1.481×10^{-2}	(1921) 1.921×10^{-2}
OGMF*, critical shear rate (1/sec)	1186	652
OGMF*, critical shear stress (MPa)	0.431	0.323
OSMF**, critical shear rate (1/sec)	about 764	about 402
OSMF**, critical shear stress (MPa)	0.366	0.280

* Onset of Gross Melt Fracture.

** Onset of Surface Melt Fracture.

The onset of gross melt fracture can easily be identified from the shear stress vs. shear rate plot shown in Figure 4 where a sudden increase of shear rate occurs at an apparent shear stress of about 3.23×10^6 dyne/cm² (0.323 MPa). A comparison of the shear stresses and corresponding shear rates before the onset of gross melt fracture is listed in

Table 4. The PI of Example 6 is surprisingly about the same as comparative example 9, v n though th 110/12 is lower for Example 6. The onset of melt fracture or sharkskin for Example 6 is also at a significantly higher shear stress and shear rate in comparison with the comparative example 9. Furthermore, it is also unexpected that the Melt Tension (MT) of Example 6 is higher than that of comparative example 9, even though the melt index for Example 6 is slightly higher and the I_{10}/I_2 is slightly lower than that of comparative example 9.

Comparative examples 10-19

Batch ethylene/1-octene polymerizations were conducted under the following conditions:

Preparation of $[\text{HNEt}_3]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$

A 100 ml flask was charged with 1.00 gram of tris(pentafluorophenyl)boron (1.95 mmol) and 70 ml of anhydrous pentane. After dissolution, 1.5 ml of MeLi (1.4 M in diethyl ether, 2.1 mmol, 1.07 equiv) was added at 25°C via syringe. A milky white mixture formed immediately and, after several minutes, two phases formed. The mixture was stirred for 15 hr and then the upper layer decanted. The viscous lower layer was washed twice with 30 ml of pentane and concentrated in vacuo for 2 hours to give a clear, colorless, viscous oil. Under nitrogen, the oil was quenched with a 40 ml of an aqueous 0.5 M HNEt₃Cl solution (20 mmol, 10 equiv) which had previously been cooled to 0°C. A white, gooey precipitate formed instantly. After two minutes, the solid was collected by filtration and washed twice with 20 ml of 0.5 M HNEt₃Cl solution followed by two washings with distilled water. The solid was dehydrated under high vacuum at 25°C for 15 hours to give a powdery white solid (0.77 grams, 63%) which was identified as the desired triethylammonium tris(pentafluorophenyl)methylborate salt.

Preparation of $[\text{HNEt}_3]^+[(\text{allyl})\text{B}(\text{C}_6\text{F}_5)_3]^-$

A 100 ml flask was charged with 1.00 gram of tris(pentafluorophenyl)boron (1.95 mmol) and 40 ml of anhydrous pentane. After dissolution, 2.05 ml of (allyl)MgBr (1.0 M in diethyl ether, 2.05 mmol, 1.05 equiv) was added at 25°C via syringe. A cloudy white mixture formed immediately and, after several minutes, two phases formed. The mixture was stirred for 15 hr and then the upper layer decanted. The viscous lower layer was washed twice with 30 ml of pentane and concentrated in vacuo for 2 hours to give a clear, colorless, viscous oil. Under nitrogen, the oil was quenched with a 40 ml of an aqueous 0.5 M HNEt₃Cl solution (20 mmol, 10 equiv) which had previously been cooled to 0°C. A gooey, white precipitate formed after several minutes. The solid was collected by filtration and washed twice with 20 ml of 0.5 M HNEt₃Cl solution followed by two washings with distilled water. The solid was dehydrated under high vacuum at 25°C for 15 hours to give a pasty white solid (0.39 grams, 30%) which was identified as the desired triethylammonium tris(pentafluorophenyl)allylborate salt.

Batch Reactor Polymerization Procedure

A 2 L stirred autoclave was charged with the desired amounts of a mixed alkane solvent (Isopar® E, available from Exxon Chemicals, Inc.) and 1-octene comonomer. The reactor was heated to the polymerization temperature. Hydrogen was added by differential pressure expansion from a 75 ml addition tank.

The term "hydrogen A psi" in Table 1 represents the difference in pressure between the starting and final pressure in the hydrogen addition tank after adding hydrogen to the 21 reactor containing a total of approximately 1200 ml of solvent and 1-octene. The reactor was heated to the polymerization temperature and was saturated with ethylene to the desired pressure. For these experiments, a constant ethylene/solvent pressure of about $3.445 \times 10^6 \text{ N/m}^2$ gauge (500 psig) at a temperature of 140°C corresponds to an ethylene concentration of about 8.4 percent by weight of the reactor contents. Metal complex and cocatalyst were mixed in a drybox by syringing the desired amount of 0.0050 M metal complex solution (in Isopar® E or toluene) into a solution of the cocatalyst (in Isopar® E or toluene). This solution was then transferred to a catalyst addition tank and injected into the reactor. The polymerization was allowed to proceed for the desired time and then the solution was drained from the bottom of the reactor and quenched with isopropanol. About 100 mg of a hindered phenolic antioxidant (Irganox® 1010, available from Ciba-Geigy corporation) was added and the polymer was air dried overnight. The residual solvent was removed in a vacuum oven overnight. The results are shown in Table 5 and 5A:

Table 5

Comp. Ex.	H ₂ ΔN/m ² (Δpsi)	1-octene (gms)	Isopar E (gms)	yield (gms)	Effcn. (gm/gm Ti)
10A*	(50) ^a	38	820	39.6	330,689
11A*	(25) ^b	38	820	70.1	390,257
12A*	(35) ^c	38	820	46.4	258,316
13A*	(30) ^d	38	820	48.8	271,677
14A*	(35) ^c	30	828	52.1	290,049
15A*	(27) ^e	38	820	36.5	152,401
16A**	(26) ^f	38	820	47.8	266,110
17B***	(35) ^c	40	818	19.7	41,127
18B***	(50) ^a	40	818	19.7	41,127
19B***	(25) ^b	40	818	18.3	38,204

A = metal complex of [(C₅Me₄)SiMe₂N(t-Bu)] TiMe₂ (as in USP '802)

B = metal complex of [(C₅Me₄)SiMe₂N(t-Bu)] TiCl₂ (as in USP '798)

* = Cocatalyst of [Et₃NH] + [(allyl)B(C₆F₅)₃]⁻ (as in USP '802)

** = Cocatalyst of [Et₃NH] + [(Me)B(C₆F₅)₃]⁻ (as in USP '802)

*** = methyl aluminoxane (MAO) (as in USP '798)

Reactor temperature is constant at about 140°C

Ethylene/solvent pressure is constant at about 3.4 x 10⁶ N/m² gauge (500 psig)

Run time is about 15 minutes

^a 0.34 x 10⁶

^b 0.17 x 10⁶

^c 0.24 x 10⁶

^d 0.21 x 10⁶

^e 0.19 x 10⁶

^f 0.18 x 10⁶

Table 5A

Comp. Ex.	μmoles complex	μmoles cocatalyst	Irganox 1010 (ppm)
10A*	2.5	2.5	2500
11A*	3.75	3.75	1400
12A*	3.75	3.75	2200
13A*	3.75	3.75	2000
14A*	3.75	3.75	1900
15A*	5	5	2700
16A**	3.75	3.75	2000
17B***	10	5000	5000
18B***	10	5000	5000
19B***	10	5000	5500

A = metal complex of [(C₅Me₄)SiMe₂N(t-Bu)] TiMe₂ (as in USP '802)

B = metal complex of [(C₅Me₄)SiMe₂N(t-Bu)] TiCl₂ (as in USP '798)

* = Cocatalyst of [Et₃NH] + [(allyl)B(C₆F₅)₃]⁻ (as in USP '802)

** = Cocatalyst of [Et₃NH] + [(Me)B(C₆F₅)₃]⁻ (as in USP '802)

*** = methyl aluminoxane (MAO) (as in USP '798)

Reactor temperature is constant at about 140°C

Ethylene/solvent pressure is constant at about 3.4 x 10⁶ N/m² gauge (500 psig)

Run time is about 15 minutes

The samples were each extruded via a Gas Extrusion Rheometer (GER) at 190°C using 0.075 cm (0.0296 inch) diameter die having UD of 20 and entrance angle of 180°, as shown in the attached drawing. The OGMF can easily

be identified from the shear stress vs. shear rate plot where a sudden jump of shear rate occurs or when the surface of the extrudate becomes very rough or irregular, or from deep ridges which can be clearly detected by visual observation. OSMF is characterized by fine scale surface irregularities ranging from loss of surface gloss to the more severe form of matte or sharkskin which can easily be seen using microscopy at a magnification of 10X.

Table 6 displays the test results from Comparative Examples 10-19:

Table 6

Comp Ex	I_2 (gm/10 min)	(I_{10}/I_2)	$(I_{10}/I_2) - 4.63$	Measured M_w/M_n	OGMF* Shear Rate (sec^{-1})	OGMF* Shear Stress (MPa)
10	4.52	5.62	0.99	1.856	706	0.344
11	0.67	6.39	1.76	1.834	118	0.323
12	2.24	5.62	0.99	1.829	300	0.323
13	2.86	5.60	0.97	1.722	397	0.323
14	3.25	5.66	1.03	1.827	445	0.302
15	1.31	5.67	1.04	1.718	227	0.302
16	1.97	5.7	1.07	1.763	275	0.302
17	0.36	12.98	8.35	5.934	<29	<0.086
18	0.40	13.34	8.71	5.148	<11.08	<0.086
19	0.13	13.25	8.62	6.824	<10.39	<0.086

Comparative Examples 10 - 16 were prepared using the catalyst composition as described in U.S. Patent 5,064,802 (Stevens et al.) as described above. Comparative Examples 17 - 19 were prepared using the catalyst composition described in U.S. Patent 5,026,798 (Canich), as described above. All of the Comparative Polymer Examples made using a batch reactor at an ethylene concentration of about 8.4 percent by weight of the reactor contents or more tested had onset of gross melt fracture at a shear stress of less than or equal to 0.344 MPa (3.44×10^6 dynes/cm²).

Interestingly, an ethylene concentration of about 8.4 percent is considered to be on the low side for a batch polymerization procedure, since it limits the reaction kinetics and slows the polymerization process. Increasing the ethylene concentration in a batch reactor, as is taught in U.S. Patent 5,026,798 (Canich), where the calculated propylene reactor concentrations for these ten examples ranges from a low of about 12.6 percent (Example 1) to a high of about 79 percent (Example 6), by weight of the reactor contents, results in polymerization of polymers which do not have the novel structure discovered by Applicants, as the OGMF data in Table 6 demonstrates. Furthermore, the 110/12 ratio of such comparative polymers made using a batch reactor at relatively high ethylene concentrations increases as the molecular weight distribution, M_w/M_n , increases, as is expected based on conventional Ziegler polymerized polymers.

Example 20 and Comparative Example 21

Blown film is fabricated from two novel ethylene/1-octene polymers made in accordance with the present invention and from two comparative conventional polymers made according to conventional Ziegler catalysis. The blown films are tested for physical properties, including heat seal strength versus heat seal temperature (shown in Figure 5 for Examples 20 and 22 and comparative examples 21 and 23), machine (MD) and cross direction (CD) properties (e.g., tensile yield and break, elongation at break and Young's modulus). Other film properties such as dart, puncture, tear, clarity, haze, 20 degree (20°) gloss and block are also tested.

Blown Film Fabrication Conditions

The improved processing substantially linear polymers of the present invention produced via the procedure described earlier, as well as two comparative resins are fabricated on an Egan blown film line using the following fabrication conditions:

- (2 inch) 5 cm diameter extruder
- (3 inch) 7.6 cm die
- 0.76 mm (30 mil) die gap
- 25 RPM extruder speed

- (460°F) 238°C melt temperatur
- 0.025 mm (1 mil) gauge
- 2.7:1 Blow up ratio (31.7 cm (12.5 inches)) layflat)
- (31.7 cm (12.5 inches)) frost line height

The melt temperature is kept constant by changing the extruder temperature profile. Frost line height is maintained at (12.5 inches) 31.7 cm by adjusting the air flow. The extruder output rate, back pressure and power consumption in amps are monitored throughout the experiment. The polymers of the present invention and the comparative polymers are all ethylene/1-octene copolymers. Table 7 summarizes physical properties of the two polymers of the invention and for the two comparative polymers:

Table 7

Property	Example 20	Comparative example 21	Example 22	Comparative example 23
I ₂ (g/10 minutes)	1	1	1	0.8
Density (g/cm ³)	0.92	0.92	0.902	0.905
I ₁₀ /I ₂	9.45	about 8	7.61	8.7
M _w /M _n	2	about 5	2	about 5

Tables 8 and 9 summarize the film properties measured for blown film made from two of these four polymers:

Table 8

Blown film properties				
Property	Example 20 MD	Example 20 CD	Comparative example 21 MD	Comparative example 21 CD
Tensile yield kPa (psi)	(1391) 9584	(1340) 9233	(1509) 10397	(1593) 10976
Tensile break kPa (psi)	(7194) 49567	(5861) 40382	(6698) 46149	(6854) 47224
Elongation (percent)	650	668	631	723
Young's modulus kPa (psi)	(18,990) 130,841	(19,997) 137,779	(23,086) 159,063	(23,524) 162,080
PPT* tear (gms)	5.9	6.8	6.4	6.5

*Puncture Propagation Tear
MD = machine direction
CD = cross direction

Table 9

Property	Example 20	Comparative example 21
Dart A (grams)	472	454
Puncture (grams)	235	275
Clarity (percent)	71	68
Haze	3.1	6.4
20° gloss	114	81
Block (grams)	148	134

During the blown film fabrication, it is noticed that at the same screw speed (25 rpm) and at the same temperature profile, the extruder back pressure is about 24115 kPa (3500 psi) at about 58 amps power consumption for comparative example 21 and about 17570 kPa (2550 psi) at about 48 amps power consumption for example 20, thus showing the novel polymer of example 20 to have improved processability over that of a conventional heterogeneous Ziegler polymerized polymer. The throughput is also higher for Example 20 than for comparative example 21 at the same screw

speed. Thus, example 20 has higher pumping efficiency than comparative example 21 (i.e., more polymer goes through per turn of the screw).

As Figure 5 shows, the heat seal properties of polymers of the present invention are improved, as evidenced by lower heat seal initiation temperatures and higher heat seal strengths at a given temperature, as compared with conventional heterogeneous polymers at about the same melt index and density.

Examples 24 and 25

The polymer products of Examples 1 and 3 are produced in a continuous solution polymerization process using a continuously stirred reactor, as described in copending U.S. application serial number 07/776,130, filed October 15, 1991. The metal complex $[C_5Me_4(SiMe_2N^iBu)]TiMe_2$ is prepared as described in copending U.S. application serial number 07/776,130 and the cocatalysts used are tris(pentafluorophenyl) borane (B:Ti ratio of 2:1) and MMAO (Al:Ti ratio of 4:1). For Example 24 the ethylene concentration in the reactor is about 1.10 percent and for Example 25 the ethylene concentration in the reactor is about 1.02 percent (percentages based on the weight of the reactor contents). For each Example, the reactor is run without hydrogen.

Additives (e.g., antioxidants, pigments, etc.) can be incorporated into the interpolymer products either during the pelletization step or after manufacture, with a subsequent re-extrusion. Examples 24 and 25 are each stabilized with 1250 ppm Calcium Stearate, 200 ppm Irganox 1010, and 1600 ppm Irgafos 168. IrgafosTM 168 is a phosphite stabilizer and IrganoxTM 1010 is a hindered polyphenol stabilizer (e.g., tetrakis [methylene 3-(3,5-ditert.butyl-4-hydroxyphenyl-propionate)]methane. Both are trademarks of and made by Ciba-Geigy Corporation.

Example 24 and Comparative Example 26

Example 24 is an ethylene/1-octene elastic substantially linear olefin polymer produced as described herein.

Comparative Example 26 is an ethylene/1-butene copolymer trademarked ExactTM made by Exxon Chemical containing butylated hydroxy toluene (BHT) and IrganoxTM 1076 as polymeric stabilizers. Table 10 summarizes physical properties and rheological performance of example 24 and comparative example 26:

Table 10

Property	Example 24	Comparative Example 26
I_2 (g/10 minutes)	3.3	3.58
Density (g/cm ³)	0.870	0.878
I_{10}/I_2	7.61	5.8
M_w/M_n	1.97	1.95
PI	3.2	8.4
N.sec/m ² (kPoise)	320	840
Elastic Modulus @ 0.1 rad/sec N.cm ² (dynes/cm ²)	(87.7) 877	(8.3) 83
OSMF*, critical shear rate (sec ⁻¹)	660	250

*Onset of surface melt fracture

Even though Example 24 and Comparative Example 26 have very similar molecular weight distributions (M_w/M_n), I_2 and density, Example 24 has a much lower processing index (PI) (38 percent of the PI of Comparative Example 26), a much higher onset of surface melt fracture (264 percent increase in OSMF) and an elastic modulus an order of magnitude higher than Comparative Example 26, demonstrating that Example 24 has much better processability and higher melt elasticity than Comparative Example 26.

Elastic modulus is indicative of a polymer's melt stability, e.g., more stable bubbles when making blown film and less neck-in. Resultant physical properties of the finished film are also higher.

Onset of surface melt fracture is easily identified by visually observing the surface extrudate and noting when the extrudate starts losing gloss and small surface roughness is detected by using 40X magnification.

Dynamic shear viscosity of the polymers is also used to show differences between the polymers and measures viscosity change versus shear rate. A Rheometrics Mechanical Spectrometer (Model RMS 800) is used to measure viscosity as a function of shear rate. The RMS 800 is used at 190°C at 15 percent strain and a frequency sweep (i.e., from 0.1-100 rad/sec) under a nitrogen purge. The parallel plates are positioned such that they have a gap of about

1.5-2 mm. Data for Example 24 and Comparative Example 26 are listed in Table 11 and graphically displayed in Figure 6.

Table 11

Shear Rate (rad/sec)	Dynamic Viscosity N.sec/m ² (poise) for Example 24	Dynamic Viscosity N.sec/m ² (poise) for Comparative Example 26
0.1	2829 (28290)	1899 (18990)
0.1585	2807 (28070)	1887 (18870)
0.2512	2763 (27630)	1895 (18950)
0.3981	2714 (27140)	1877 (18870)
0.631	2645 (26450)	1884 (18840)
1	2556 (25560)	1880 (18800)
1.585	2444 (24440)	1869 (18690)
2.512	2314 (23140)	1854 (18540)
3.981	2170 (21700)	1796 (17960)
6.31	2017 (20170)	1796 (17960)
10	1853 (18530)	1744 (17440)
15.85	1679 (16790)	1666 (16660)
25.12	1496 (14960)	1562 (15620)
39.81	1307 (13070)	1431 (14310)
63.1	1118 (11180)	1275 (12750)
100	928 (9280)	1096 (10960)

Surprisingly, Example 24 shows a shear thinning behaviour, even though Example 24 has a narrow molecular weight distribution. In contrast, Comparative Example 26 shows the expected behaviour of a narrow molecular weight distribution polymer, with a flatter viscosity/shear rate curve.

Thus, elastic substantially linear olefin polymers made in accordance with the present invention (e.g. Example 24) have lower melt viscosity than a typical narrow molecular weight distribution linear copolymer made by single site catalyst technology at the melt processing shear rate region of commercial interest. In addition, the novel elastic substantially linear olefin polymers have a higher low shear/zero shear viscosity than the Comparative linear polymer, thus demonstrating that the copolymers of the invention have higher "green strength" which is useful for forming and maintaining blended compositions such as those used in the wire and cable coating industry, where the compounded materials must maintain their integrity at low or zero shear without segregating the components.

Example 25 and Comparative Example 27

Example 25 is an ethylene/1-octene elastic substantially linear olefin polymer produced in a continuous solution polymerization process as described herein.

Comparative Example 27 is an ethylene/propene copolymer made by Mitsui PetroChemical Corporation and trademarked Tafmer™ P-0480. Table 12 summarizes physical properties and rheological performance of these two polymers:

Table 12

Property	Example 25	Comparative Example 27
I ₂ (g/10 minutes)	1.01	1.1
Density (g/cm ³)	0.870	0.870
I ₁₀ /I ₂	7.62	6.06
M _w /M _n	1.98	1.90

Table 12 (continued)

Property	Example 25	Comparative Example 27
PI	7.9	27.4
N.sec/m ² (kPoise)	790	2740
Elastic Modulus @ 0.1 rad/sec	964	567.7
N.cm ² (dynes/cm ²)	9640	5677
OSMF*, critical shear rate (sec ⁻¹)	781	105

*Onset of surface melt fracture

Even though Example 25 and Comparative Example 27 have similarly narrow molecular weight distributions (M_w/M_n), I_2 , and density, Example 25 has a PI which is 28 percent of that of Comparative Example 27, a 743 percent increase in onset of surface melt fracture and a higher elastic modulus than Comparative Example 27, demonstrating that Example 24 has much better processability than Comparative Example 27. Onset of surface melt fracture is easily identified by visually observing the surface extrudate and noting when the extrudate starts losing gloss and small surface roughness is detected by using 40X magnification.

Examples 28-37

Examples 28-35 are ethylene/propene copolymers made using the constrained geometry catalyst described herein and in a continuous solution polymerization process. Examples 36 and 37 are ethylene/1-butene copolymers made using the constrained geometry catalyst described herein and in a continuous solution polymerization process. Examples 28-35 each contained approximately 1250 ppm calcium stearate and 200 ppm Irganox 1010. Table 13 and 13A describe the polymerization conditions and Table 14 describes the resultant polymer physical properties for Examples 28-35:

Table 13

Ex.	Reactor ethylene conc. (weight percent)	Estimated reactor PE conc. (weight percent)	Ethylene flow rate (lbs/ hr) kg/hr	Hydrogen/ethylene ratio (mole percent)
28	5.3	6.0	(3.19) 1.44	0.048
29	4.2	7.3	(3.19) 1.44	0.024
30	4.0	8.9	(3.19) 1.44	0.028
31	3.5	9.3	(3.18) 1.43	0.024
32	2.5	10.6	(3.20) 1.44	0.027
33	2.6	10.7	(3.18) 1.43	0.007
34	1.3	10.5	(3.19) 1.44	0.027
35	1.0	10.9	(3.19) 1.44	0.010

Table 13A

Ex.	Reactor temp (°C)	Diluent/ethylene ratio	Comonomer/olefin ratio
2	170	8.2	25.5

Table 13A (continued)

Ex.	Reactor temp (°C)	Diluent/ethylene ratio	Comonomer/olefin ratio
8			
2 9	172	8.1	24.0
3 0	171	7.1	16.6
3 1	171	7.2	20.1
3 2	170	7.1	15.6
3 3	173	7.1	16.7
3 4	145	8.2	17.8
3 5	158	8.2	18.8

Table 14

Ex.	I_2 (gms/10 minutes)	I_{10}/I_2	Density (gm/cm ³)	M_w/M_n
28	1.08	7.8	0.9176	2.00
29	1.02	8.8	0.9173	2.17
30	0.82	9.2	0.9175	2.08
31	0.79	9.4	0.9196	2.04
32	1.01	10.6	0.9217	2.09
33	0.83	12.4	0.9174	2.31
34	0.54	15.2	0.9201	2.12
35	0.62	15.6	0.9185	2.32

Figure 7 graphically displays a best fit line drawn through a plot of the I_{10}/I_2 ratio for the ethylene/propene substantially linear polymers of examples 28-35 as a function of ethylene concentration in the polymerization reactor. Surprisingly, in contrast to conventional Ziegler polymerized polymers and in contrast to a batch polymerization using the same catalyst and relatively high ethylene concentrations, as the ethylene concentration in the reactor decreases using a continuous polymerization process, the I_{10}/I_2 ratio (indicating the amount of long chain branching in the novel substantially linear polymers) increases, even though the molecular weight distribution, M_w/M_n , remains very narrow and essentially constant at about 2.

Table 15 shows the critical shear stress and critical shear rate at OGMF and OSMF for examples 28-35:

Table 15

Example	OSMF (N.cm ²)	OGMF (N.cm ²)
28 (shear stress)	21.5 (2.15×10^6) dynes/cm ²	40.9 (4.09×10^6) dynes/cm ²
28 (shear rate)	129.8 sec ⁻¹	668.34 sec ⁻¹
29 (shear stress)	19.4 (1.94×10^6) dynes/cm ²	43 (4.3×10^6) dynes/cm ²
29 (shear rate)	118.8 sec ⁻¹	652.1 sec ⁻¹
30 (shear stress)	10.8 (1.08×10^6) dynes/cm ²	43 (4.3×10^6) dynes/cm ²

Table 15 (continued)

Exmpl	OSMF (N.cm ²)	OGMF (N.cm ²)
30 (shear rate)	86.12 sec ⁻¹	650.7 s c ⁻¹
31 (shear stress)	10.8 (1.08 x 10 ⁶) dynes/cm ²	>43 (>4.3 x 10 ⁶) dynes/cm ²
31 (shear rate)	90.45 sec ⁻¹	>683 sec ⁻¹
32 (shear stress)	19.4 (1.94 x 10 ⁶) dynes/cm ²	36.6 (3.66 x 10 ⁶) dynes/cm ²
32 (shear rate)	178.2 sec ⁻¹	673 sec ⁻¹
33 (shear stress)	21.5 (2.15 x 10 ⁶) dynes/cm ²	about 32.3 (3.23 x 10 ⁶) dynes/cm ²
33 (shear rate)	235.7 sec ⁻¹	about 591 sec ⁻¹
34 (shear stress)	19.4 (1.94 x 10 ⁶) dynes/cm ²	34.4 (3.44 x 10 ⁶) dynes/cm ²
34 (shear rate)	204.13 sec ⁻¹	725.23 sec ⁻¹
35 (shear stress)	19.4 (1.94 x 10 ⁶) dynes/cm ²	about 32.6 (3.26 x 10 ⁶) dynes/cm ²
35 (shear rate)	274.46 sec ⁻¹	637.7 sec ⁻¹

Table 16 and 16A describe the polymerization conditions and Table 17 describes the resultant polymer physical properties for ethylene/1-butene copolymer Examples 36 and 37:

Table 16

Ex.	Reactor ethylene conc. (weight percent)	Reactor PE conc (weight percent)	Ethylene flow rate (lbs/ hr) kg/hr	Hydrogen/ethylene ratio (mole percent)
36	5.3	5.8	3.20 1.44	0.035
37	1.3	10.8	3.19 1.44	0.010

Table 16A

Ex.	Reactor temp (°C)	Diluent/ethylene ratio	Comonomer/olefin ratio
36	170	8.1	24.2
37	152	8.2	17.1

Table 17

Ex.	I ₂ (gms/10 minutes)	I ₁₀ /I ₂	Density (gm/cm ³)	M _w /M _n
36	0.59	7.5	0.9201	2.06
37	1.03	11.4	0.9146	2.22

The data in Tables 16, 16A and 17 show that as the ethylene concentration in the reactor decreases while using the constrained geometry catalyst as described herein, the I₁₀/I₂ ratio of the novel substantially linear polymers increases, indicating the amount of long chain branching in the novel polymers, even while the molecular weight distribution, Mw/Mn, of the novel polymers remains narrow at essentially about 2.

Table 18 shows the critical shear stress and critical shear rate at OGMF and OSMF for examples 36 and 37:

Table 18

Example	OGMF (N.cm ²)	OSMF (N.cm ²)
36 (shear stress)	19.4 (1.94 x 10 ⁶) dynes/cm ²	40.9 (4.09 x 10 ⁶) dynes/cm ²

Table 18 (continued)

Example	OGMF (N.cm ²)	OSMF (N.cm ²)
36 (shear rate)	52.3 sec ⁻¹	234.45 sec ⁻¹
37 (shear stress)	10.8 (1.08 x 10 ⁶) dynes/cm ²	30.1 (3.01 x 10 ⁶) dynes/cm ²
37 (shear rate)	160.5 sec ⁻¹	493.9 sec ⁻¹

Proposed Example 38

Example 4 is essentially repeated except that propylene is substituted for ethylene in the polymerization.

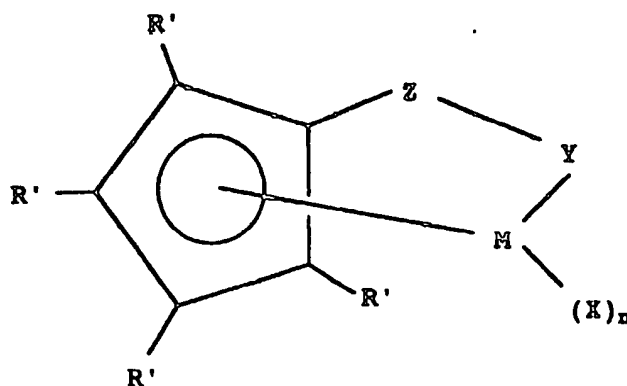
Proposed Example 39

Example 1 is essentially repeated except that propylene is copolymerized with at least one C₂-C₂₀ α-olefin in the polymerization.

Claims

1. An olefin polymer characterized in that the olefin polymer is an olefin polymer, substituted with 0.01 to 3 long chain branches per 1000 carbons of the backbone, having a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer that does not have long chain branches at about the same I_2 and M_w/M_n , and has a single melting point as determined by differential scanning calorimetry.
2. The polymer of claim 1, having
 - a) a melt flow ratio $I_1/I_2 \geq 5.63$, and
 - b) a molecular weight distribution, M_w/M_n , defined by the equation $M_w/M_n \leq (I_1/I_2) - 4.63$.
3. The polymer of claim 1 or 2, having a critical shear stress at onset of gross melt fracture greater than 40 N/cm² (4 x 10⁶ dyne/cm²).
4. The polymer of any one of the claims 1-3, having a molecular weight distribution, M_w/M_n , of less than 5.
5. The polymer of any one of the claims 1-4, having a molecular weight distribution, M_w/M_n , of less than 3.5.
6. The polymer of any one of the claims 1-5, having a molecular weight distribution, M_w/M_n , from 1.5 to 2.5.
7. The polymer of any one of the claims 1-6, having from 0.01 to 1 long chain branches/1000 carbons along the polymer backbone.
8. The polymer of any one of the preceding claims, which is:
 - (A) a homopolymer of a C₂-C₂₀ olefin, or
 - (B) an interpolymer of ethylene with at least one C₂-C₂₀ acetylenically unsaturated monomer, or
 - (C) an interpolymer of ethylene with at least one C₄-C₁₈ diolefin, or
 - (D) an interpolymer of ethylene with at least one C₃-C₂₀ α-olefin and at least one C₄₋₁₈ diolefin.
9. The polymer of any one of the preceding claims, which is:
 - (A) an ethylene homopolymer, or
 - (B) an interpolymer of ethylene with at least one C₃-C₂₀ α-olefin.
10. The polymer of any one of the preceding claims, wherein the polymer is an ethylene polymer.

11. The polymer of any one of the preceding claims, being a copolymer of ethylene and 1-octene.
12. A process for the preparation of an olefin polymer substituted with 0.01 to 3 long chain branches per 1000 carbons of the backbone, having a melt flow ratio $I_{10}/I_2 \geq 5.63$, a molecular weight distribution M_w/M_n defined by the equation $M_w/M_n \leq I_{10}/I_2 - 4.63$, and a single melting point as determined by differential scanning calorimetry, said process being characterized as a continuous process comprising continuously contacting one or more C_2 - C_{20} olefins with a catalyst composition under polymerization conditions, wherein said catalyst composition is characterized as:
- one metal coordination complex comprising a metal atom of groups 3-10 or the Lanthanide series of the Periodic Table of the Elements and a delocalized π -bonded moiety substituted with a constrain inducing moiety, said complex having a constrained geometry about the metal atom such that the angle at the metal atom between the centroid of the delocalized, substituted π -bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar π -bonded moiety lacking in such constrain-inducing substituent, and provided further that for such complexes comprising more than one delocalized, substituted π -bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted π -bonded moiety, and
 - an activating cocatalyst.
13. The continuous process of claim 12, wherein the metal coordination complex corresponds to the formula:

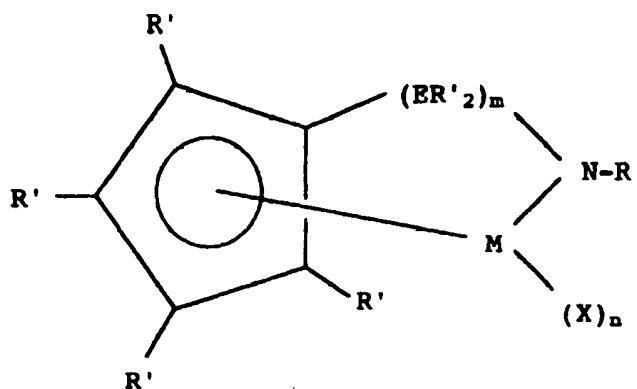


wherein R' each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, germyl, cyano, halo and combinations thereof having up to 20 non-hydrogen atoms; X each occurrence independently is selected from the group consisting of hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, neutral Lewis base ligands and combinations thereof having up to 20 non-hydrogen atoms; Y is $-O-$, $-S-$, $-NR^*$, $-PR^*$ or a neutral two electron donor ligand selected from the group consisting of $-OR^*$, $-SR^*$, $-NR^*_2$ and $-PR^*_2$;

M is a metal of Group 3-10, or the Lanthanide series of the Periodic Table of the Elements and preferably Ti ; and Z is SiR^*_2 , CR^*_2 , $SiR^*_2SiR^*_2$, $CR^*_2CR^*_2$, $CR^*=CR^*$, $CR^*_2SiR^*_2$, GeR^*_2 , BR^* , BR^*_2 ; wherein

R^* each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 non-hydrogen atoms, and mixtures thereof, or two or more R^* groups from Y , Z , or both Y and Z form a fused ring system; and n is 1 or 2.

14. The continuous process of claim 12, wherein a) is an amidosilane- or amidoalkanediy- compound corresponding to the formula:



wherein M is titanium, zirconium or hafnium, bound to an η^5 -cyclopentadienyl group;
 R' each occurrence is independently selected from hydrogen, silyl, alkyl, aryl and combinations thereof having
 up to 10 carbon and/or silicon atoms;

E is silicon or carbon;

X independently each occurrence is a hydride, alkyl or aryl of up to 20 carbons; and
 m is 1 or 2.

15. The continuous process of any one of claims 12-14, wherein b) is

- (A) methylaluminoxane or
- (B) tris(pentafluorophenyl)borane.

16. The continuous process of any one of claims 12-15, wherein the process is:

- (A) a gas phase process, or
- (B) a suspension process, or
- (C) a solution process, or
- (D) a slurry process.

17. The continuous process of any one of claims 12-16, wherein the polymerization conditions comprise a reaction temperature and olefin concentration sufficient to form an olefin polymer according to claim 1 having a I_{10}/I_2 of at least 8.

18. The continuous process of any one of claims 12-17, wherein the polymerization conditions comprise a reaction temperature and olefin concentration sufficient to form an olefin polymer according to claim 1 having a I_{10}/I_2 of at least 9.

19. The continuous process of any one of claims 12-18, wherein

- (A) the one or more C_{2-20} olefins are ethylene or ethylene in combination with at least one C_{3-20} α -olefin; and
- (B) said ethylene polymer is recovered;

wherein said ethylene polymer is characterized as an ethylene polymer substituted with 0.01 to 3 long chain branches per 1000 carbons of the backbone having a melt flow ration $I_{10}/I_2 \geq 5.63$, and a molecular weight distribution M_w/M_n defined by the equation $M_w/M_n \leq (I_{10}/I_2) - 4.63$, and a single melting point as determined using differential scanning calorimetry.

20. The continuous process of claim 19, wherein the ethylene concentration is further characterized as not more than 8 percent of the reactor contents to form an ethylene polymer substituted with 0.01 to 3 long chain branches per 1000 carbons of the backbone having a I_{10}/I_2 of at least 8.

21. The continuous process of claim 19 or 20, wherein the ethylene concentration is further characterized as not more

than 6 percent of the reactor contents to form an ethylene polymer substituted with 0.1 to 3 long chain branches per 1000 carbons of the backbone having a I_{10}/I_2 of at least 9.

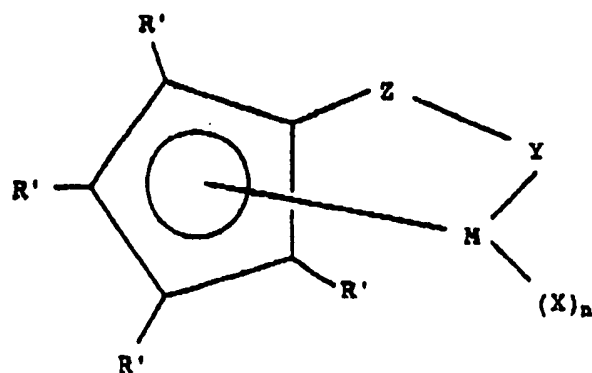
22. The continuous process of any one of claims 19-21, wherein ethylene is contacted with 1-propene, 1-butene, 1-hexene, 4-methyl-1-pentene or 1-octene.
23. The continuous process of claim 22, being a solution process.
24. The continuous process of claim 23, wherein the ethylene is contacted with 1-octene.
25. The continuous process of claim 19 or claim 22, being a gas phase process.
26. The polymer obtainable by the continuous process of any one of claims 12-25.
27. A composition comprising one olefin polymer of any of claims 1-11 and at least one other natural or synthetic polymer.
28. The composition of claim 27 wherein the olefin polymer is
 - (A) an ethylene/ α -olefin polymer, or
 - (B) an ethylene homopolymer.
29. The composition of claim 27 or 28, wherein the synthetic polymer is a conventional Ziegler polymerized ethylene/ α -olefin polymer.
30. A fabricated article comprising the olefin polymer of any one of claims 1-11.
31. The fabricated article of claim 30, being a film, a fiber, a sheet, a woven fabric, a non-woven fabric, a molded article or a wire and cable coating.
32. The fabricated article of claim 31, wherein the film is a blown film.
33. The blown film of claim 32, wherein the olefin polymer is an ethylene/ α -olefin copolymer having a density of from 0.9 g/cm³ to 0.92 g/cm³.
34. The blown film of claim 33, wherein the ethylene/ α -olefin copolymer has a molecular weight distribution M_w/M_n of from 1.5 to 2.5.
35. The blown film of claim 34, wherein the film has a heat seal strength equal to or higher than a film made from a heterogeneous Ziegler polymerized polymer at the same heat seal temperature, wherein the ethylene/ α -olefin copolymer and the heterogeneous Ziegler polymerized polymer have about the same melt index and about the same density.

Patentansprüche

1. Olefinpolymeres, dadurch gekennzeichnet, daß das Olefinpolymere ein mit 0,01 bis 3 langkettigen Verzweigungen pro 1000 Kohlenstoffen des Rückgrates substituiertes Olefinpolymeres ist, das eine kritische Scherrate bei Beginn des Oberflächenschmelzbruchs von wenigstens 50 % größer als die kritische Scherrate beim Beginn des Oberflächenschmelzbruchs eines linearen Olefinpolymeren, das keine langkettigen Verzweigungen aufweist, bei etwa denselben I_2 und M_w/M_n hat und einen einzigen Schmelzpunkt, bestimmt durch Differentialabstakalorimetrie, besitzt.
2. Polymeres nach Anspruch 1, mit
 - a) einem Schmelzflußverhältnis $I_{10}/I_2 \geq 5,63$, und
 - b) einer Molekulargewichtsverteilung, M_w/M_n , definiert durch die Gleichung $M_w/M_n \geq I_{10}/I_2 - 4,63$.

3. Polymeres nach Anspruch 1 oder 2, mit einer kritischen Scherspannung beim Beginn des Gesamtschmelzbruchs größer als 40 N/cm^2 ($4 \times 10^6 \text{ dyn/cm}^2$).
- 5 4. Polymeres nach einem der Ansprüche 1 - 3, mit einer Molekulargewichtsverteilung, M_w/M_n , von weniger als 5.
5. Polymeres nach einem der Ansprüche 1 - 4, mit einer Molekulargewichtsverteilung, M_w/M_n , von weniger als 3,5.
6. Polymeres nach einem der Ansprüche 1 - 5, mit einer Molekulargewichtsverteilung, M_w/M_n , von 1,5 bis 2,5.
- 10 7. Polymeres nach einem der Ansprüche 1 - 6, mit von 0,01 bis 1 langkettigen Verzweigungen/1000 Kohlenstoffen längs dem Polymerrückgrat.
8. Polymeres nach einem der vorhergehenden Ansprüche, welches ist:
 - 15 (A) ein Homopolymeres eines C_2 - C_{20} -Olefins, oder
 - (B) ein Interpolymeres von Ethylen mit wenigstens einem acetylenartig ungesättigten C_2 - C_{20} -Monomeren, oder
 - (C) ein Interpolymeres von Ethylen mit wenigstens einem C_4 - C_{18} -Diolefin, oder
 - 20 (D) ein Interpolymeres von Ethylen mit wenigstens einem C_3 - C_{20} - α -Olefin und wenigstens einem C_4 - C_{18} -Diolefin.
9. Polymeres nach einem der vorhergehenden Ansprüche, welches ist:
 - 25 (A) ein Ethylenhomopolymeres, oder
 - (B) ein Interpolymeres von Ethylen mit wenigstens einem C_3 - C_{20} - α -Olefin.
10. Polymeres nach einem der vorhergehenden Ansprüche, worin das Polymere ein Ethylenpolymeres ist.
11. Polymeres nach einem der vorhergehenden Ansprüche, welches ein Copolymeres von Ethylen und 1-Octen ist.
- 30 12. Verfahren zur Herstellung eines Olefinpolymeren, das mit 0,01 bis 3 langkettigen Verzweigungen pro 1000 Kohlenstoffen des Rückgrates substituiert ist, mit einem Schmelzflußverhältnis $I_1/I_2 \geq 5,63$, einer Molekulargewichtsverteilung, M_w/M_n , definiert durch die Gleichung $M_w/M_n \leq I_1/I_2 - 4,63$ und einem einzigen Schmelzpunkt, bestimmt durch Differentialabtauskalorimetrie, wobei dieses Verfahren als ein kontinuierliches Verfahren gekennzeichnet ist, welches das kontinuierliche Inkontaktbringen von einem oder mehreren C_2 - C_{20} -olefinen mit einer Katalysatorzusammensetzung unter Polymerisationsbedingungen umfaßt, worin diese Katalysatorzusammensetzung gekennzeichnet ist als:
 - 40 a) ein Metallkoordinationskomplex, umfassend ein Metallatom der Gruppen 3 - 10 oder der Lanthanidenreihen des Periodensystems der Elemente und eine delokalisierte π -gebundene Einheit, die mit einer Spannung induzierenden Einheit substituiert ist, wobei dieser Komplex eine um das Metallatom derart gespannte Geometrie besitzt, daß der Winkel an dem Metallatom zwischen dem Schwerpunkt der delokalisierten substituierten π -gebundenen Einheit und dem Zentrum von wenigstens einem verbleibenden Substituenten geringer als ein solcher Winkel in einem ähnlichen Komplex ist, der eine ähnliche π -gebundene Einheit enthält, der ein solche Spannung induzierender Substituent fehlt, und vorausgesetzt ferner, daß für solche Komplexe, die mehr als eine delokalisierte substituierte π -gebundene Einheit umfassen, nur eine hiervon für jedes Metallatom des Komplexes eine cyclische delokalisierte substituierte π -gebundene Einheit ist, und
 - 45 b) ein aktivierender Cokatalysator.
- 50 13. Kontinuierliches Verfahren nach Anspruch 12, worin der Metallkoordinationskomplex der Formel entspricht:

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worin R' bei jedem Vorkommen unabhängig ausgewählt ist aus der Gruppe, bestehend aus Wasserstoff, Alkyl, Aryl, Silyl, Germyl, Cyano, Halogen und Kombinationen hiervon, die bis zu 20 Nicht-Wasserstoffatome hat; X bei jedem Vorkommen unabhängig ausgewählt ist aus der Gruppe, bestehend aus Hydrid, Halogen, Alkyl, Aryl, Silyl, Germyl, Aryloxy, Alkoxy, Amid, Siloxy, neutralen Lewisbasen-liganden und Kombinationen, die bis zu 20 Nicht-Wasserstoffatome hat;

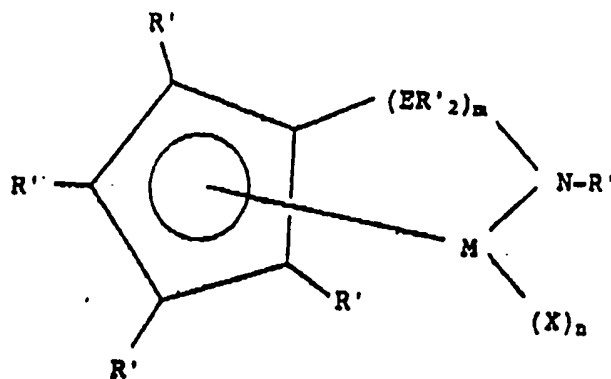
Y = -O-, -S-, -NR*, -PR*, oder ein neutraler Zweielektronendonorligand, ausgewählt aus der aus -OR*, -SR*, -NR*₂ und -PR*₂ bestehenden Gruppe, ist;

M ein Metall der Gruppe 3 - 10 oder der Lanthanidenreihen des Periodensystems der Elemente und bevorzugt Ti ist; und

Z = SiR*₂, CR*₂, SiR*₂SiR*₂, CR*₂CR*₂, CR*=CR*, CR*₂SiR*₂, GeR*₂, BR*, BR*₂ ist, worin R* bei jedem Vorkommen unabhängig ausgewählt ist aus der Gruppe, bestehend aus Wasserstoff, Alkyl-, Aryl-, Silyl-, halogenierten Alkyl-, halogenierten Arylgruppen, welche bis zu 20 Nicht-Wasserstoffatome haben, oder Mischungen hiervon, oder zwei oder mehr R*-Gruppen von Y, Z oder beiden Y und Z ein kondensiertes Ringsystem bilden, und

n = 1 oder 2 ist.

14. Kontinuierliches Verfahren nach Anspruch 12, worin a) eine Amidosilan- oder Amidoalkandiyilverbindung ist, die der Formel entspricht:



worin M = Titan, Zirkonium oder Hafnium, gebunden an eine η^5 -Cyclopentadienylgruppe, ist;

R' bei jedem Vorkommen unabhängig ausgewählt ist aus Wasserstoff, Silyl, Alkyl, Aryl und Kombinationen hiervon mit bis zu 10 Kohlenstoff- und/oder Siliziumatomen;

E = Silizium oder Kohlenstoff ist;

X unabhängig bei jedem Vorkommen ein Hydrid, Alkyl oder Aryl von bis zu 20 Kohlenstoffen ist; und

m = 1 oder 2 ist.

15. Kontinuierliches Verfahren nach einem der Ansprüche 12 - 14, worin b) ist:

- (A) Methylaluminiumoxan oder
- (B) Tris-(pentafluorphenyl)-boran.

16. Kontinuierliches Verfahren nach einem der Ansprüche 12 - 15, worin das Verfahren ist:

- (A) ein Gasphasenverfahren, oder
- (B) ein Suspensionsverfahren, oder
- (C) ein Lösungsverfahren, oder
- (D) ein Aufschlammungsverfahren.

17. Kontinuierliches Verfahren nach einem der Ansprüche 12 - 16, worin die Polymerisationsbedingungen eine Reaktionstemperatur und eine Olefinkonzentration umfassen, die zur Bildung eines Olefinpolymeren nach Anspruch 1 mit einem I_{10}/I_2 von wenigstens 8 ausreichen.

18. Kontinuierliches Verfahren nach einem der Ansprüche 12 - 17, worin die Polymerisationsbedingungen eine Reaktionstemperatur und eine Olefinkonzentration umfassen, die zur Bildung eines Olefinpolymeren nach Anspruch 1 mit einem I_{10}/I_2 von wenigstens 9 ausreichen.

19. Kontinuierliches Verfahren nach einem der Ansprüche 12 - 18, worin

- (A) das eine oder die mehreren Olefin/e Ethylen oder Ethylen in Kombination mit wenigstens einem C_3 - C_{20} - α -Olefin ist/sind;
- (B) dieses Ethylenpolymere gewonnen wird;

worin dieses Ethylenpolymere gekennzeichnet ist als ein Ethylenpolymeres, das mit 0,01 bis 3 langkettigen Verzweigungen pro 1000 Kohlenstoffen des Rückgrates substituiert ist, mit einem Schmelzflußverhältnis $I_{10}/I_2 \geq 5,63$, einer Molekulargewichtsverteilung, M_w/M_n , definiert durch die Gleichung $M_w/M_n \leq I_{10}/I_2 - 4,63$, und einem einzigen Schmelzpunkt, bestimmt durch Differentialabtauskalorimetrie.

20. Kontinuierliches Verfahren nach Anspruch 19, worin die Ethylenkonzentration weiter gekennzeichnet ist als nicht mehr als 8 % der Reaktorinhalte zur Bildung eines Ethylenpolymeren, das mit 0,01 bis 3 langkettigen Verzweigungen pro 1000 Kohlenstoffen des Rückgrates substituiert ist, mit einem I_{10}/I_2 von wenigstens 8.

21. Kontinuierliches Verfahren nach Anspruch 19 oder 20, worin die Ethylenkonzentration weiter gekennzeichnet ist als nicht mehr als 6 % der Reaktorinhalte zur Bildung eines Ethylenpolymeren, das mit 0,01 bis 3 langkettigen Verzweigungen pro 1000 Kohlenstoffen des Rückgrates substituiert ist, mit einem I_{10}/I_2 von wenigstens 9.

22. Kontinuierliches Verfahren nach einem der Ansprüche 19 - 21, worin Ethylen mit 1-Propen, 1-Buten, 1-Hexen, 4-Methyl-1-penten oder 1-Octen in Kontakt gebracht wird.

23. Kontinuierliches Verfahren nach Anspruch 22, welches ein Lösungsverfahren ist.

24. Kontinuierliches Verfahren nach Anspruch 23, worin das Ethylen mit 1-Octen in Kontakt gebracht wird.

25. Kontinuierliches Verfahren nach Anspruch 19 oder Anspruch 22, welches ein Gasphasenverfahren ist.

26. Polymeres, erhältlich nach dem kontinuierlichen Verfahren eines der Ansprüche 12 - 25.

27. Zusammensetzung, umfassend ein Olefinpolymeres eines der Ansprüche 1 - 11 und wenigstens ein anderes natürliches oder synthetisches Polymeres.

28. Zusammensetzung nach Anspruch 27, worin das Olefinpolymere ist:

- (A) ein Ethylen/ α -Olefinpolymeres, oder
- (B) ein Ethylenhomopolymeres.

29. Zusammensetzung nach Anspruch 27 oder 28, worin das synthetische Polymere ein konventionelles Ziegler-polymerisiertes Ethylen/ α -Olefinpolymeres ist.

30. Hergestellter Artikel, umfassend das Olefinpolymere von einem der Ansprüche 1 - 11.
31. Hergestellter Artikel nach Anspruch 30, der eine Folie, eine Faser, eine Platte, ein gewebtes Material ein nichtgewebtes Material, in Formgegenstand oder eine Draht- und Kabelummantelung ist.
32. Hergestellter Gegenstand nach Anspruch 31 worin die Folie eine Blasfolie ist.
33. Blasfolie nach Anspruch 32, worin das Olefinpolymere ein Ethylen/ α -Olefinocopolymeres mit einer Dichte von 0,9 g/cm³ bis 0,92 g/cm³ ist.
34. Blasfolie nach Anspruch 33, worin das Ethylen/ α -Olefinocopolymere eine Molekulargewichtsverteilung M_w/M_n von 1,5 bis 2,5 besitzt.
35. Blasfolie nach Anspruch 34, worin die Folie eine Heißsiegelfestigkeit gleich oder höher als eine Folie, die aus einem heterogenen Ziegler-polymerisierten Polymeren hergestellt ist, bei derselben Heißsiegeltemperatur hat, wobei das Ethylen/ α -Olefinocopolymere und das heterogene Ziegler-polymerisierte Polymere etwa denselben Schmelzindex und etwa dieselbe Dichte besitzen.

Revendications

1. Polyoléfine caractérisée en ce que la polyoléfine est une polyoléfine substituée par 0,01 à 3 ramifications à chaîne longue pour 1000 atomes de carbone du squelette, présentant une vitesse de cisaillement critique au début de la fracture en surface à l'état fondu, supérieure d'au moins 50 % à la vitesse de cisaillement critique au début de la fracture en surface à l'état fondu d'une polyoléfine linéaire qui ne présente pas de ramifications à chaîne longue pour environ les mêmes I_2 et M_p/M_n , et présente un point de fusion unique tel que déterminé par analyse calorimétrique différentielle (DSC).
2. Polymère conforme à la revendication 1, qui présente :
 - a) un rapport d'indices de fluidité à chaud $I_{10}/I_2 \geq 5,63$, et
 - b) un indice de polymolécularité, M_p/M_n , défini par l'équation $M_p/M_n \leq (I_{10}/I_2) - 4,63$.
3. Polymère conforme à la revendication 1 ou 2, qui présente une contrainte de cisaillement critique au début de la fracture globale à l'état fondu, supérieure à 40 N/cm² (4×10^6 dyne/cm²).
4. Polymère conforme à l'une quelconque des revendications 1 à 3, qui présente un indice de polymolécularité, M_p/M_n , inférieur à 5.
5. Polymère conforme à l'une quelconque des revendications 1 à 4, qui présente un indice de polymolécularité, M_p/M_n , inférieur à 3,5.
6. Polymère conforme à l'une quelconque des revendications 1 à 5, qui présente un indice de polymolécularité, M_p/M_n , compris entre 1,5 et 2,5.
7. Polymère conforme à l'une quelconque des revendications 1 à 6, qui présente de 0,01 à 1 ramification à longue chaîne pour 1000 atomes de carbone le long du squelette du polymère.
8. Polymère conforme à l'une quelconque des précédentes revendications, qui est :
 - (A) un homopolymère d'une oléfine en C₂-C₂₀, ou
 - (B) un interpolymère d'éthylène avec au moins un monomère en C₂-C₂₀ à insaturation acétylénique, ou
 - (C) un interpolymère d'éthylène avec au moins une dioléfine en C₄-C₁₈, ou
 - (D) un interpolymère d'éthylène avec au moins une α -oléfine en C₃-C₂₀ et au moins une dioléfine en C₄-18.
9. Polymère conforme à l'une quelconque des précédentes revendications, qui est :
 - (A) un homopolymère d'éthylène, ou

(B) un interpolymère d'éthylène avec au moins une α -oléfine en C_3 - C_{20} .

10. Polymère conforme à l'une quelconque des précédentes revendications, dans lequel le polymère est un polyéthylène.

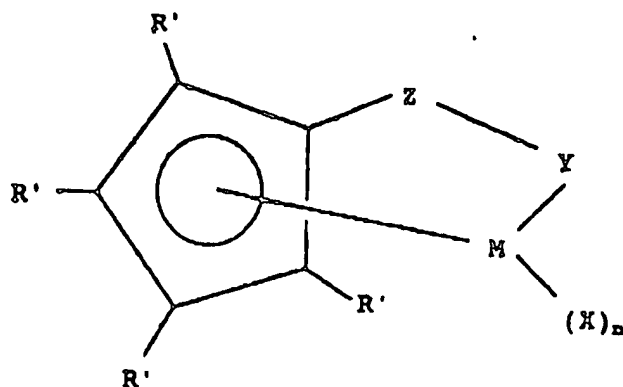
11. Polymère conforme à l'une quelconque des précédentes revendications, qui est un copolymère d'éthylène et de 1-octène.

12. Procédé pour préparer une polyoléfine substituée par 0,01 à 3 ramifications à longue chaîne pour 1000 atomes de carbone du squelette, qui présente un rapport d'indices de fluidité à chaud $I_{10}/I_2 \geq 5,63$, un indice de polymolécularité, M_p/M_n , défini par l'équation $M_p/M_n \leq (I_{10}/I_2) - 4,63$, et un point de fusion unique tel que déterminé par analyse calorimétrique différentielle (DSC), ledit procédé étant caractérisé comme un procédé continu comprenant le fait de mettre en continu une ou plusieurs oléfines en C_2 - C_{20} en contact avec une composition de catalyseur dans des conditions de polymérisation, dans lequel ladite composition de catalyseur est caractérisé par :

a) un complexe de coordination métallique qui comprend un atome de métal des Groupes 3 à 10 ou de la série des lanthanides de la Classification Périodique des Éléments, et un groupe lié par l'intermédiaire du système π délocalisé et substitué par un groupe induisant une contrainte, ledit complexe présentant une géométrie de contrainte en ce qui concerne l'atome de métal, telle que l'angle au niveau de l'atome de métal entre le centre de masse du groupe substitué et lié par l'intermédiaire du système π délocalisé, et le centre d'au moins l'un des substituants restants, soit inférieur à l'angle en question dans un complexe similaire contenant un groupe similaire lié par liaison π , mais qui ne contient pas un tel substituant induisant une contrainte, et en outre, à condition que pour de tels complexes comprenant plus d'un groupe substitué et lié par l'intermédiaire du système π délocalisé, un seul de ces groupes pour chaque atome de métal du complexe est un groupe cyclique substitué et lié par l'intermédiaire du système π délocalisé, et

b) un cocatalyseur d'activation.

13. Procédé continu conforme à la revendication 12, dans lequel le complexe de coordination métallique répond à la formule :



dans laquelle chaque R' est indépendamment choisi dans l'ensemble constitué par un atome d'hydrogène, les groupes alkyle, aryle, silyle, germyle, cyano, halogéno et leurs combinaisons comportant jusqu'à 20 atomes qui ne sont pas des atomes d'hydrogène ;

chaque X est indépendamment choisi dans l'ensemble constitué par les groupes hydrure, halogéno, alkyle, aryle, silyle, germyle, aryloxy, alcoxy, amide, siloxy, ligands neutres de bases de Lewis et leurs combinaisons comportant jusqu'à 20 atomes qui ne sont pas des atomes d'hydrogène ;

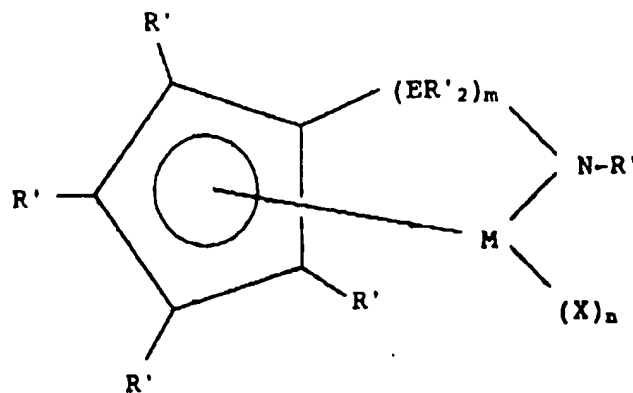
Y représente $-O-$, $-S-$, $-NR^*$, $-PR^*$ ou un ligand neutre donneur de deux électrons, choisi dans l'ensemble constitué par $-OR^*$, $-SR^*$, $-NR^*_2$ et $-PR^*_2$;

M représente un atome de métal des Groupes 3 à 10 ou de la série des lanthanides de la Classification Périodique des Éléments, et de préférence représente Ti ; et

Z représente SiR^*_2 , CR^*_2 , $SiR^*_2SiR^*_2$, $CR^*_2CR^*_2$, $CR^*=CR^*$, $CR^*_2SiR^*_2$, GeR^*_2 , BR^* , BR^*_2 dans lesquels : chaque R^* est indépendamment choisi dans l'ensemble constitué par un atome d'hydrogène, les groupes alkyle, aryle, silyle, alkyle halogéné, aryle halogéné, comportant jusqu'à 20 atomes qui ne sont pas des atomes

d'hydrogène, et leurs mélanges, ou deux ou plus de deux groupes R* dans Y, dans Z ou à la fois dans Y et Z forment un système cyclique condensé ; et n vaut 1 ou 2.

14. Procédé continu conforme à la revendication 12, dans lequel a) est un composé de type amidosilane ou amidoalcanediyle répondant à la formule :



dans laquelle M représente un atome de titane, de zirconium ou d'hafnium, lié à un groupe η^5 -cyclopentadiényle ;
chaque R' est indépendamment choisi parmi un atome d'hydrogène, les groupes silyle, alkyle, aryle et leurs combinaisons comportant jusqu'à 10 atomes de carbone et/ou atomes de silicium ;
E représente un atome de silicium ou de carbone ;
chaque X représente un groupe hydrure, alkyle ou aryle comportant jusqu'à 20 atomes de carbone ; et m vaut 1 ou 2.

15. Procédé continu conforme à l'une quelconque des revendications 12 à 14, dans lequel b) est :

(A) le méthylaluminoxane, ou
(B) le tris(pentafluorophényl)borane.

16. Procédé continu conforme à l'une quelconque des revendications 12 à 15, dans lequel le procédé est :

(A) un procédé en phase gazeuse, ou
(B) un procédé en suspension, ou
(C) un procédé en solution, ou
(D) un procédé en émulsion.

17. Procédé continu conforme à l'une quelconque des revendications 12 à 16, dans lequel les conditions de polymérisation comprennent une température de réaction et une concentration d'oléfine suffisantes pour former une polyoléfine conforme à la revendication 1, présentant un I_1/I_2 d'au moins 8.

18. Procédé continu conforme à l'une quelconque des revendications 12 à 17, dans lequel les conditions de polymérisation comprennent une température de réaction et une concentration d'oléfine suffisantes pour former une polyoléfine conforme à la revendication 1, présentant un I_1/I_2 d'au moins 9.

19. Procédé continu conforme à l'une quelconque des revendications 12 à 18, dans lequel :

(A) la ou les polyoléfines en C_{2-20} sont l'éthylène ou l'éthylène en combinaison avec au moins une α -oléfine en C_{3-20} ; et
(B) on récupère ledit polyéthylène ;

dans lequel ledit polyéthylène est caractérisé comme étant un polyéthylène substitué par 0,01 à 3 ramifications à

chaîne longue pour 1000 atomes de carbone du squelette, présentant un rapport d'indices de fluidité à chaud $I_{10}/I_2 \geq 5,63$, un indice de polymolécularité, M_p/M_n , défini par l'équation $M_p/M_n \leq (I_{10}/I_2 - 4,63)$, et un point de fusion unique tel que déterminé par analyse calorimétrique différentielle (DSC).

- 5 20. Procédé continu conforme à la revendication 19, dans lequel la concentration d'éthylène est de plus caractérisé comme ne dépassant pas 8 % du contenu du réacteur pour former un polyéthylène substitué par 0,01 à 3 ramifications à chaîne longue pour 1000 atomes de carbone du squelette, présentant un I_{10}/I_2 d'au moins 8.
- 10 21. Procédé continu conforme à la revendication 19 ou 20, dans lequel la concentration d'éthylène est de plus caractérisé comme ne dépassant pas 6 % du contenu du réacteur pour former un polyéthylène substitué par 0,01 à 3 ramifications à chaîne longue pour 1000 atomes de carbone du squelette, présentant un I_{10}/I_2 d'au moins 9.
- 15 22. Procédé continu conforme à l'une quelconque des revendications 19 à 21, dans lequel on met l'éthylène en contact avec le 1-propène, 1-butène, 1-hexène, 4-méthyl-1-pentène ou 1-octène.
- 20 23. Procédé continu conforme à la revendication 22, qui est un procédé en solution.
24. Procédé continu conforme à la revendication 23, dans lequel on met l'éthylène en contact avec le 1-octène.
- 25 25. Procédé continu conforme à la revendication 19 ou 22, qui est un procédé en phase gazeuse.
26. Polymère pouvant être obtenu par le procédé continu conforme à l'une quelconque des revendications 12 à 25.
27. Composition comprenant une polyoléfine conforme à l'une quelconque des revendications 1 à 11, et au moins un autre polymère naturel ou synthétique.
28. Composition conforme à la revendication 27, dans laquelle la polyoléfine est :
 - (A) un polymère éthylène/ α -oléfine, ou
 - (B) un homopolymère d'éthylène.
29. Composition conforme à la revendication 27 ou 28, dans laquelle le polymère synthétique est un polymère éthylène/ α -oléfine résultant de la polymérisation classique de Ziegler.
- 30 30. Article fabriqué comprenant la polyoléfine conforme à l'une quelconque des revendications 1 à 11.
31. Article fabriqué conforme à la revendication 30, qui est un film, une fibre, une feuille, un tissu tissé, un tissu non-tissé, un article moulé ou un revêtement de fil ou de câble.
32. Article fabriqué conforme à la revendication 31, dans lequel le film est un film formé par soufflage.
33. Film formé par soufflage conforme à la revendication 32, dans lequel la polyoléfine est un copolymère éthylène/ α -oléfine présentant une masse volumique de 0,9 g/cm³ à 0,92 g/cm³.
34. Film formé par soufflage conforme à la revendication 33, dans lequel le copolymère éthylène/ α -oléfine présente un indice de polymolécularité M_p/M_n compris entre 1,5 et 2,5.
- 35 35. Film formé par soufflage conforme à la revendication 34, dans lequel le film présente une résistance au scellage à chaud supérieure ou égale à celle d'un film en polymère résultant de la polymérisation hétérogène de Ziegler, à la même température de scellage à chaud, dans lequel le copolymère éthylène/ α -oléfine et le polymère résultant de la polymérisation hétérogène de Ziegler présentent environ le même indice de fluidité à chaud et environ la même masse volumique.

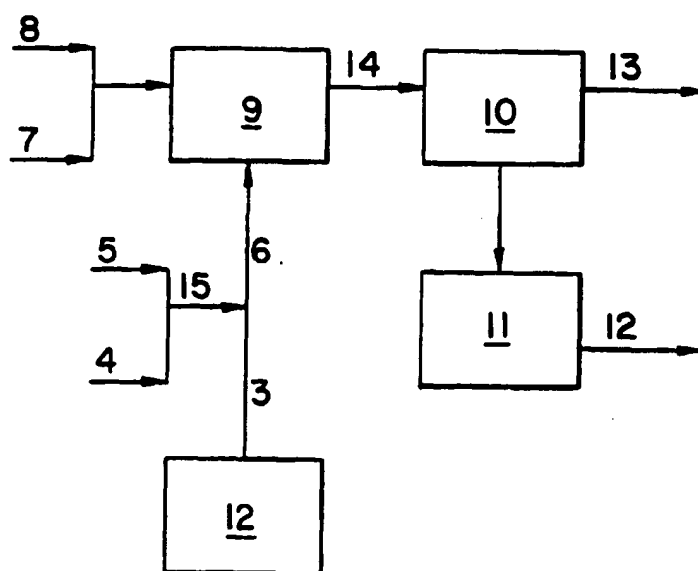


FIG. 1

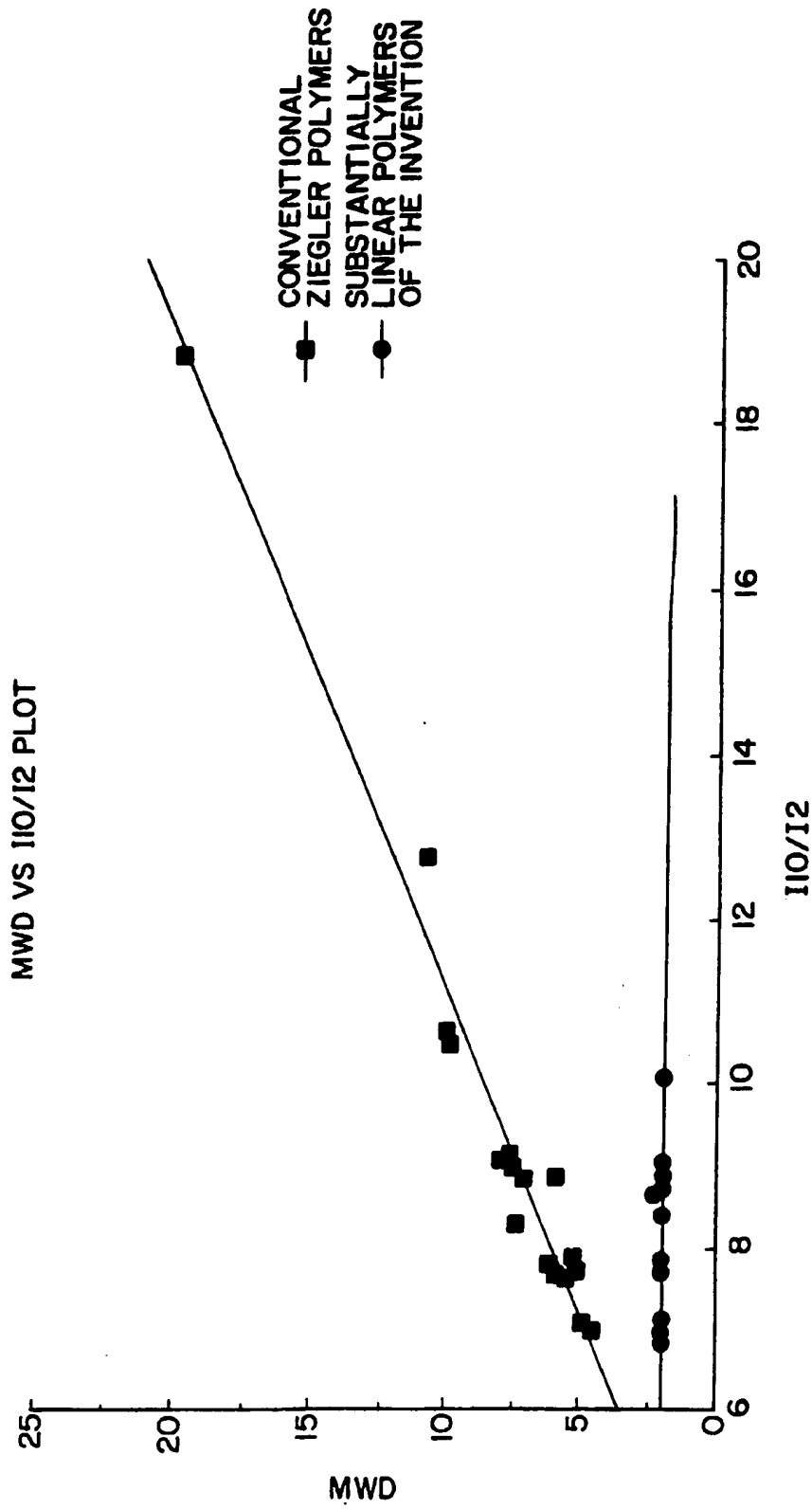


FIG. 2

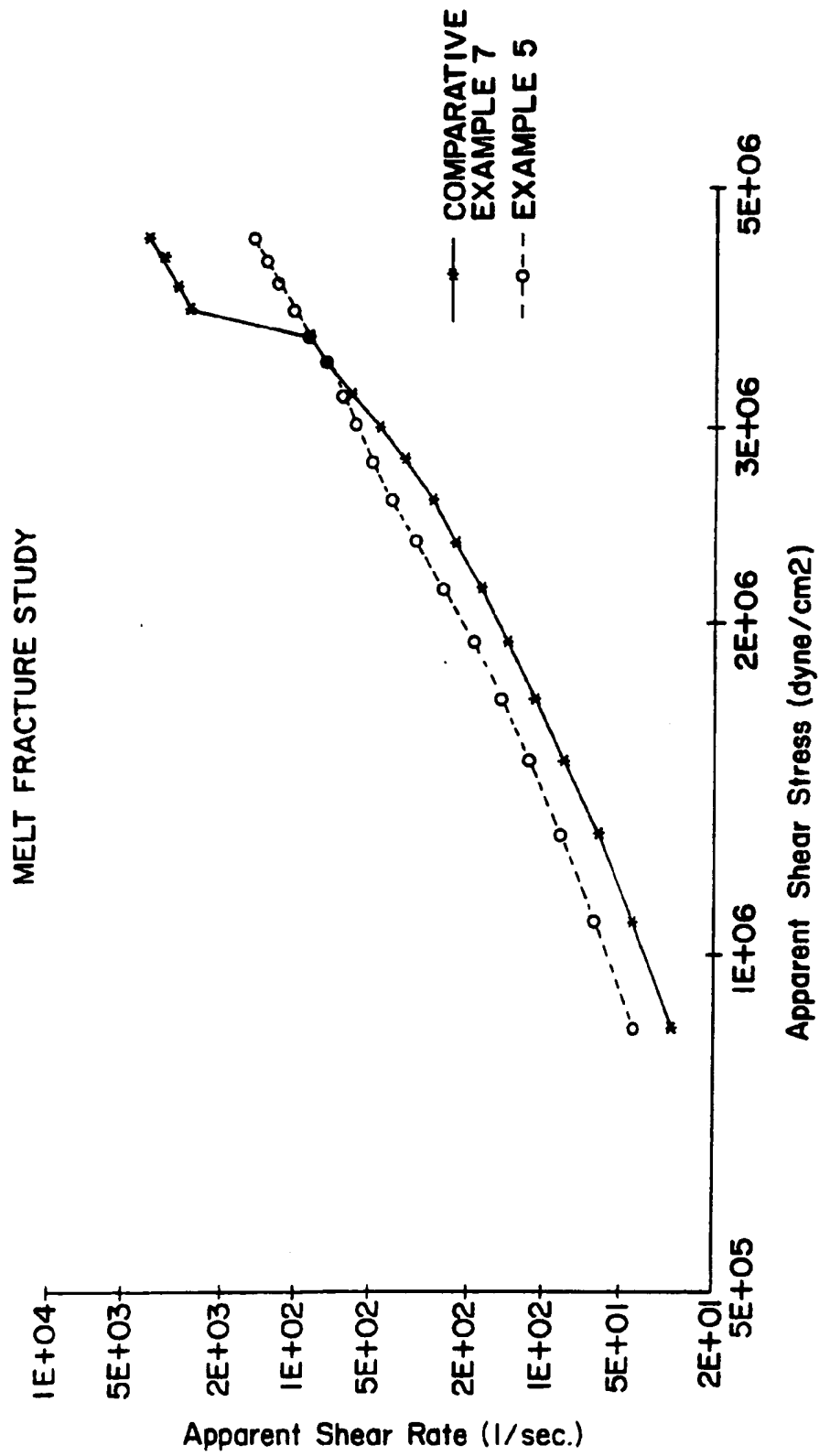


FIG. 3

MELT FRACTURE STUDY

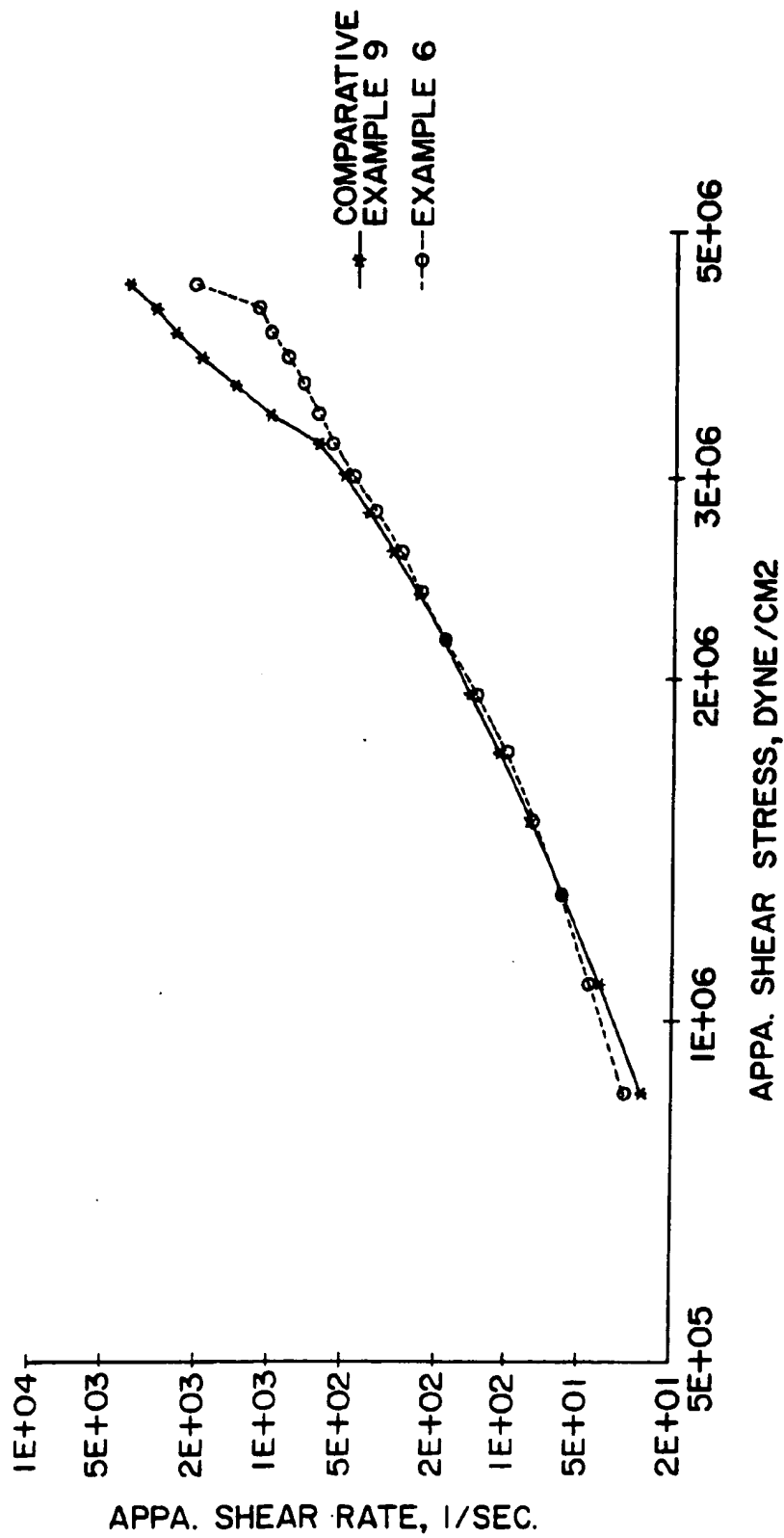


FIG.4

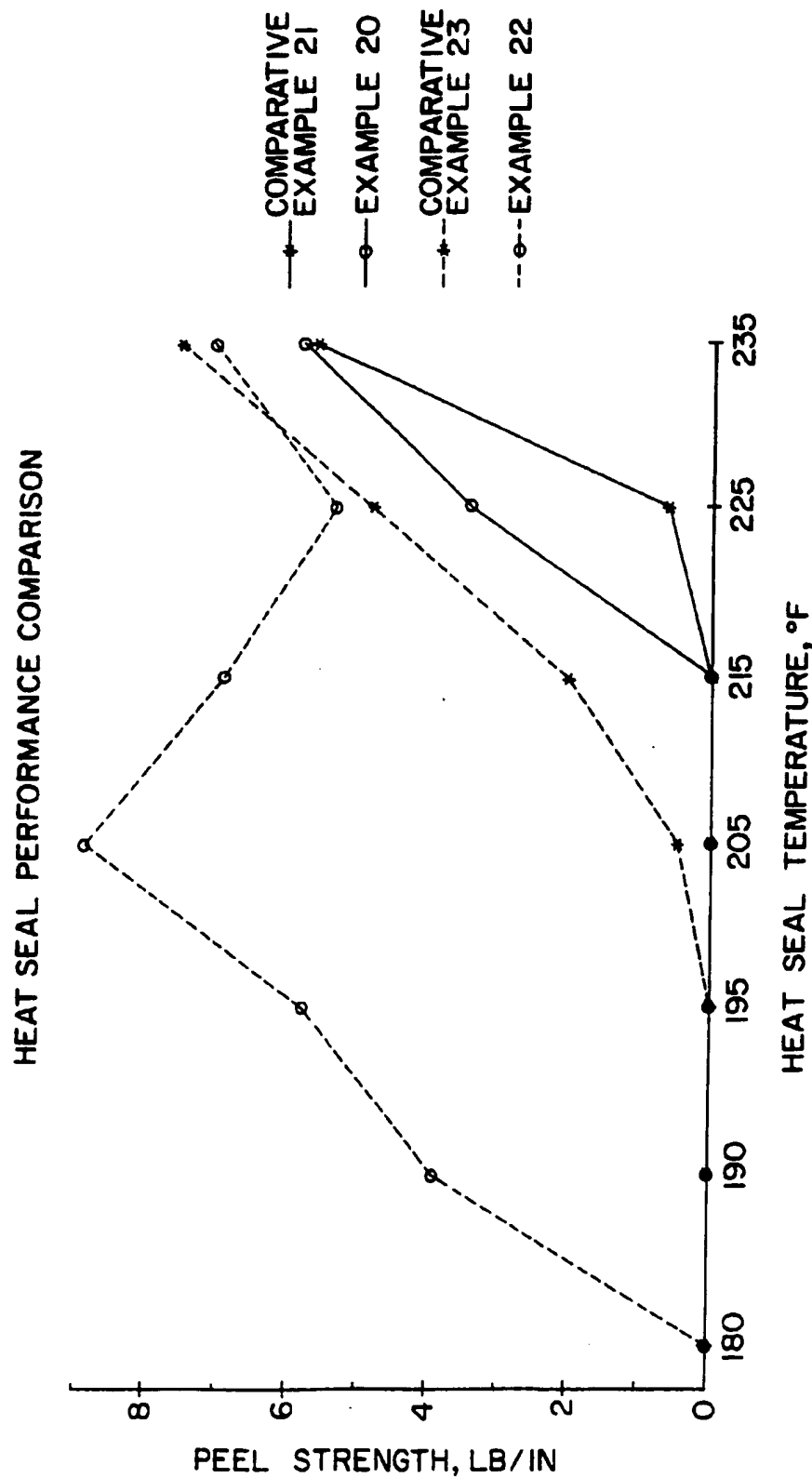


FIG.5

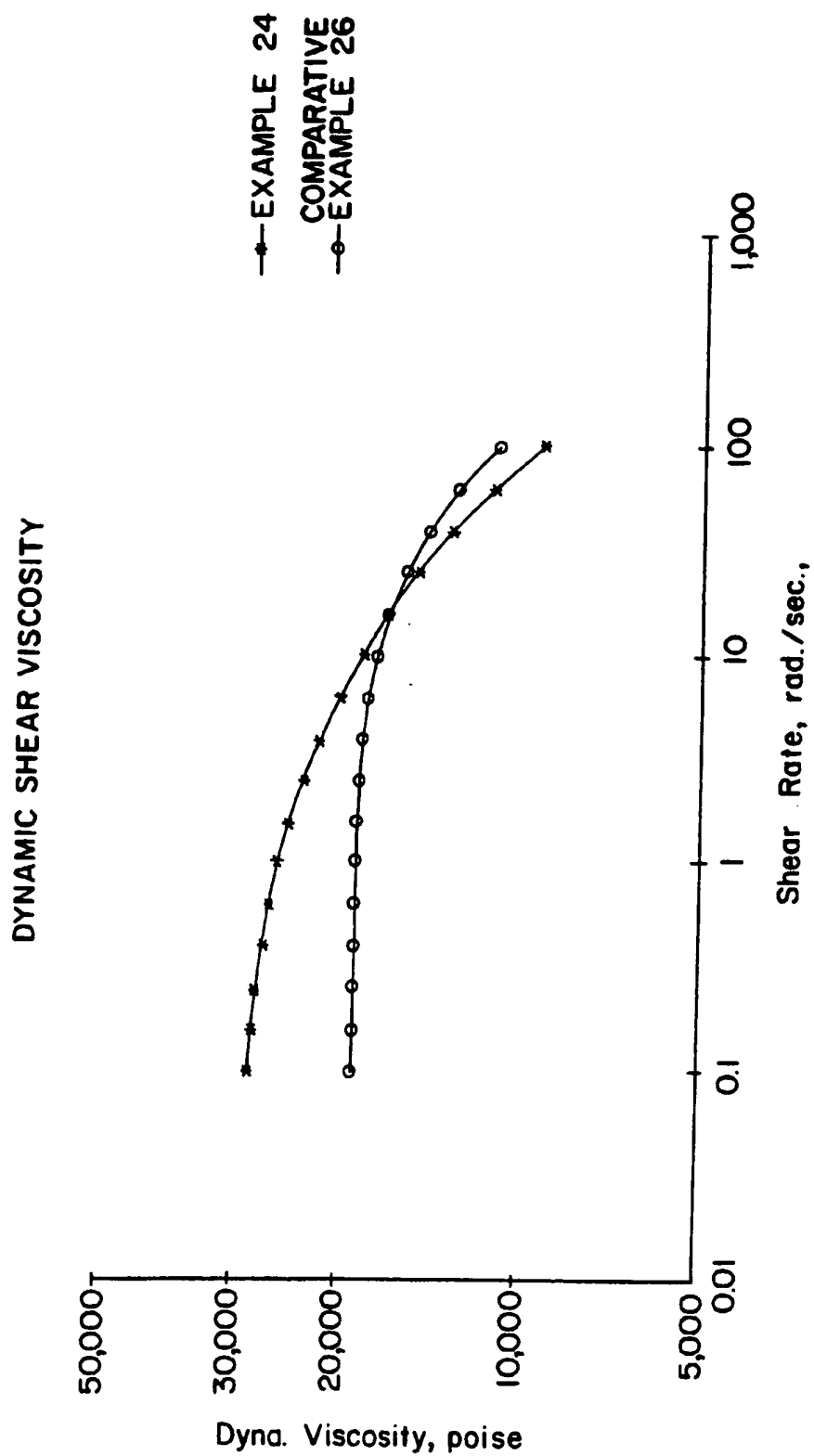


FIG.6

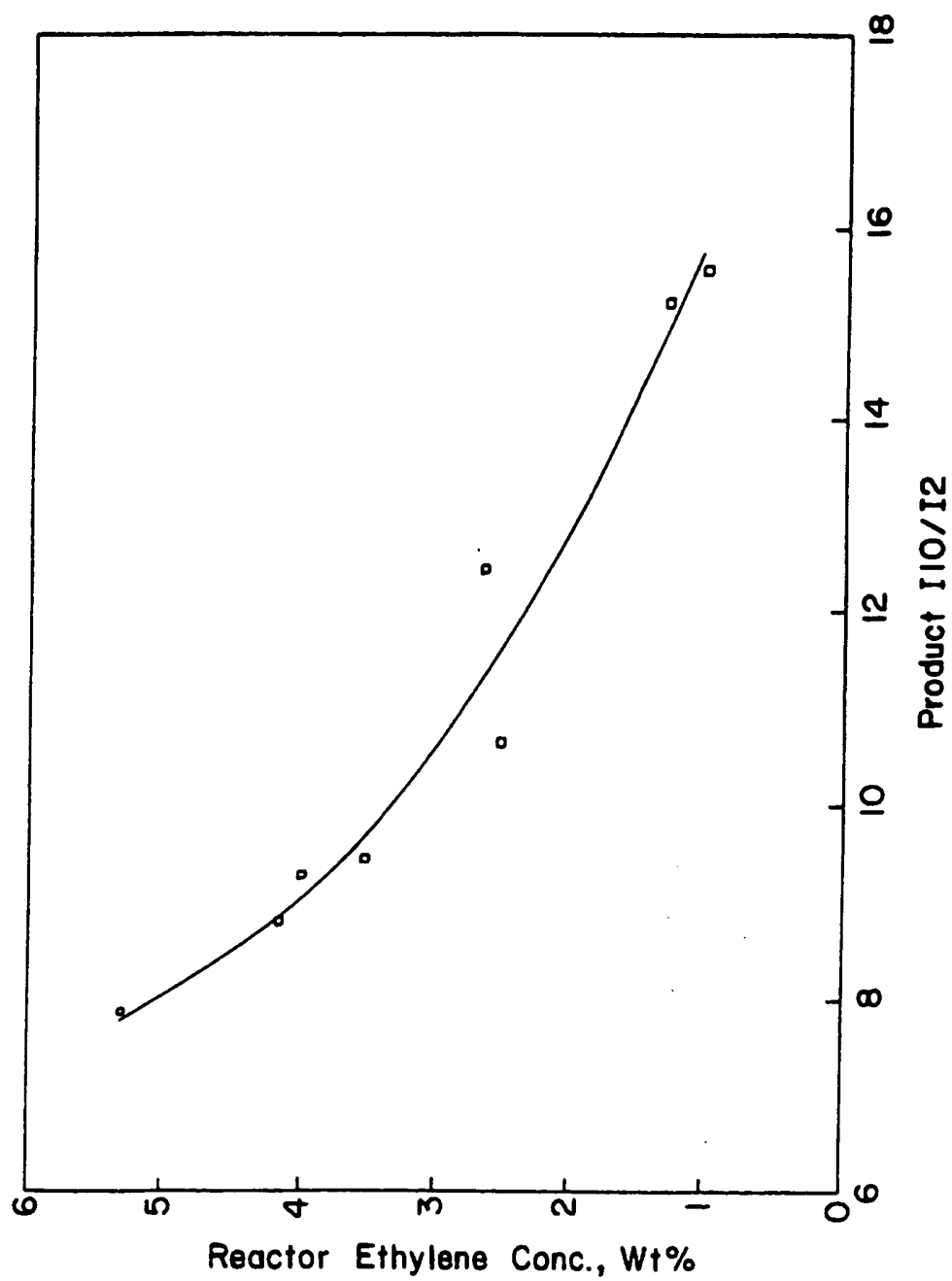


FIG.7